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Laboratory Evaluation of Level 1 Organic Analysis Procedures

Arthur D. Little, Inc.
Cambridge, MA

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Laboratory Evaluation of Level 1 Organic Analysis Procedures

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16. ABSTRACT The report describes an evaluation of the Level 1 organic sampling and analysis procedures proposed in 'IERL-RTP Procedures Manual: Level 1 Environmental Assessment,' EPA-600/2-76-160a, June 1976. (This manual has been superseded by EPA-600/7-78-201, October 1978.) Priorities of the study included: development of a resource of information concerning the behavior of compounds and classes of compounds when subjected to Level 1 procedures, and identification of problems and limitations of the proposed procedures that might require revision in methodology. The report gives results of a series of experimental studies of the organic analysis procedures as proposed and as eventually modified. Laboratory studies are described in discrete independent chapters that deal with the individual experimental investigations.

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ABSTRACT

Level 1 is the first stage in a three-tiered approach to performing an environmental source assessment. Level 1 is designed to provide enough information about the composition of effluent and process streams to permit them to be ranked in order of priority for probable environmental hazard. A set of sampling and analysis procedures designed to achieve these objectives was developed and published in an EPA report in June, 1976. That methodology was based on previously available laboratory procedures, which had not, however, been specifically tested to determine their suitability for this particular purpose. The overall objective of the work described in this report was to evaluate the Level 1 organic sampling and analysis procedures as proposed in the June, 1976 manual. Priorities of this study included: the development of a resource of information concerning the behavior of compounds and classes of compounds when subjected to Level 1 procedures; and identification of problems and limitations of the proposed procedures that might require revisions in methodology. This report presents the results of a series of experimental studies of the organic analysis procedures as proposed and as eventually modified. The report also includes several examples of Level 1 organic analysis data for samples analyzed according to the revised procedures. The results for a coal sample, a fuel oil sample, and a SASS train sample of an actual emission source are presented in the Level 1 report format.

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I. INTRODUCTION

The Process Measurement Branch of IERL/RTP has developed a three-tiered or phased approach to performing an environmental source assessment. The phased sampling and analytical strategy was developed to focus available resources (both manpower and dollars) on emissions that have a high potential for causing measurable health or ecological effects, and to provide comprehensive chemical and biological information on all sources of industrial emissions.

The phased approach requires three separate levels of sampling and analytical effort. The first, Level 1, is designed to provide enough information about the composition of effluent and process streams to permit them to be ranked in order of priority for probable environmental hazard. The Level 1 assessment is intended to: 1) provide preliminary environmental assessment data, 2) identify principal problem areas, and 3) provide the data needed for prioritization of energy and industrial processes, streams within a process, components within a stream, and classes of materials, for further consideration in the overall assessment. The second phase of sampling and analysis effort, Level 2, is designed to provide additional information that will confirm and expand the information gathered in Level 1. The third phase, Level 3, will permit quantitative monitoring of specific pollutants identified in Level 2.

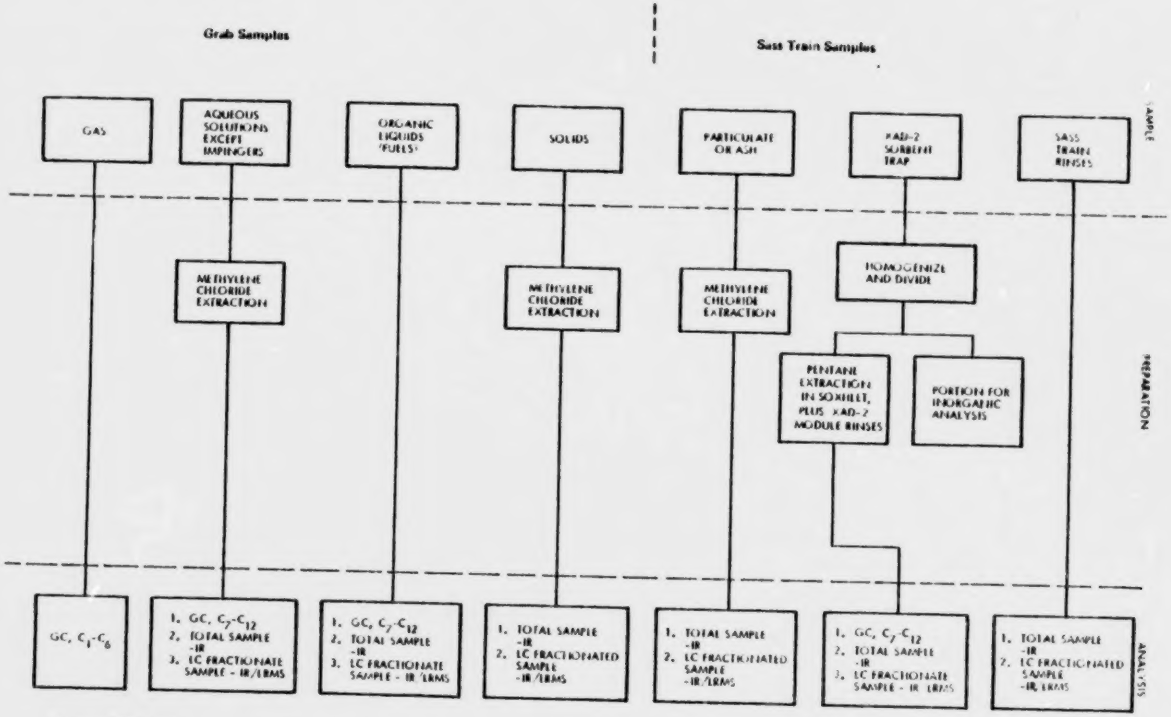
A set of sampling and analysis procedures designed to achieve the objectives of Level 1 environmental assessment was developed and published in an EPA report in June, 1976. (1) The methodology selected was based on previously available laboratory procedures. However, time constraints mitigated against experimental investigation of the entire, integrated protocol prior to its initial publication. The Level 1 procedures are comprehensive, covering inorganic and organic chemical analysis, and biological testing.

The overall objective of the work described in this report was to evaluate the Level 1 organic sampling and analysis procedures as proposed in the June, 1976 manual. Priorities of this study included: development of a resource of information concerning the behavior of compounds and classes of compounds when subjected to Level 1 procedures; and identification of problems and limitations of the proposed procedures that might require revision in methodology. The question of stability of Level 1 samples collected for organic analysis has been addressed in two separate studies (2,3).

The Level 1 organic analysis methodology is designed to identify the major classes of organic compounds present in a process or effluent stream and to estimate their concentrations. The overall organic procedures as originally proposed are summarized in Figure 1 (sampling) and Figure 2 (analysis).

This report presents the results of a series of experimental studies of the organic analysis procedures as proposed and as eventually modified. Laboratory studies are described here in discrete independent chapters that deal with the individual experimental investigations. The topics are presented in an order that seems to be logical in retrospect. The experimental work was carried out at Arthur D. Little, Inc. over the period January, 1977 to December, 1978 and documented in monthly progress reports. An integrated overview of the evaluated and revised procedures can be found in Chapter 9 of the second edition of the Level 1 Procedures Manual (4). For convenience, that chapter is reproduced as Appendix A of this report.

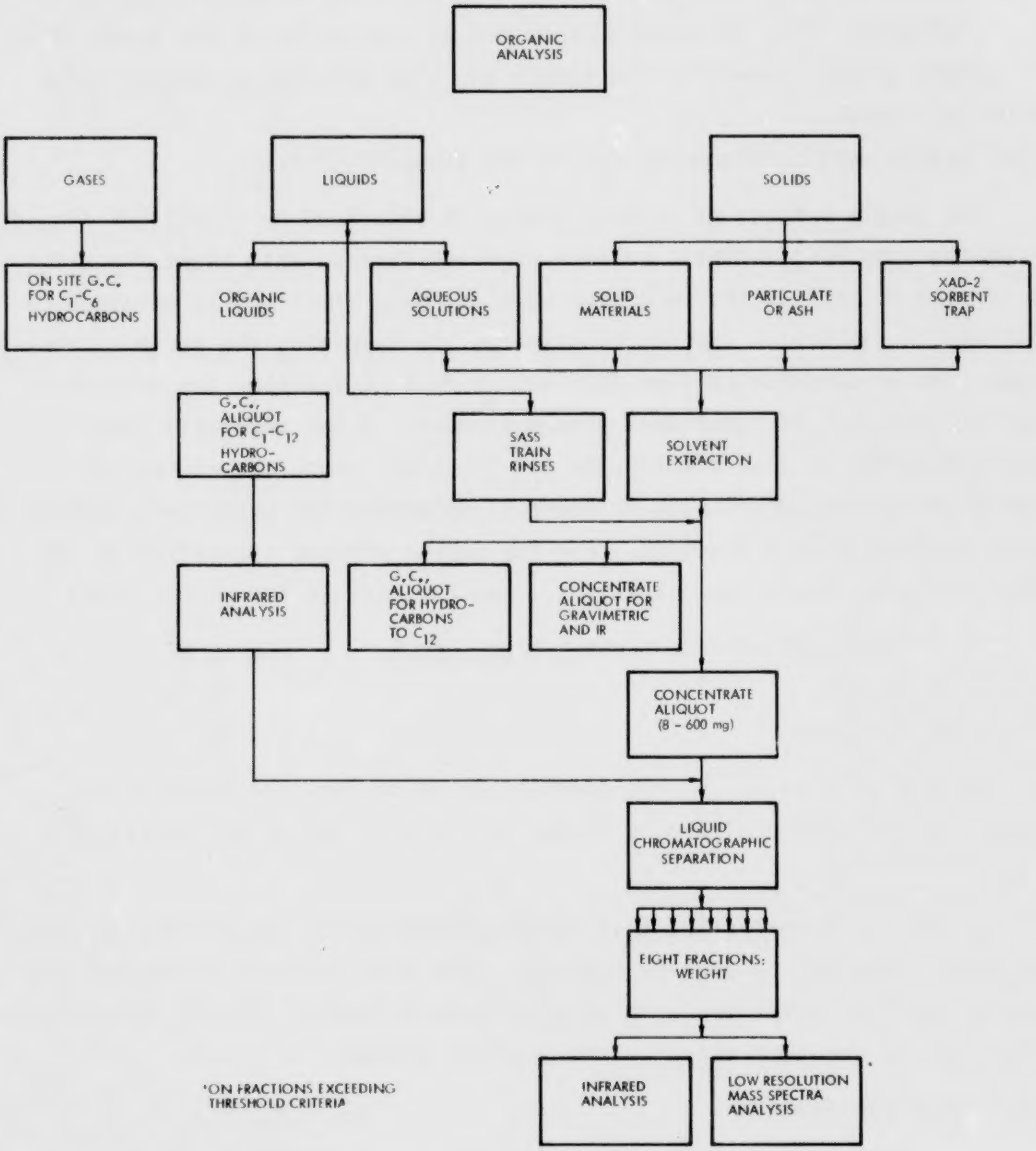
This report also includes several examples of Level 1 organic analysis data for samples analyzed according to the revised procedures. The results for a coal sample and a fuel oil sample and a SASS train sample of an actual emission source are presented in the Level 1 report format.



Grab Samples
Sass Train Samples
SAMPLE
PREPARATION
ANALYSIS
GAS
AQUEOUS SOLUTIONS EXCEPT IMPINGERS
ORGANIC LIQUIDS 'FUELS'
SOLIDS
PARTICULATE OR ASH
XAD-2 SORBENT TRAP
SASS TRAIN RINSES
METHYLENE CHLORIDE EXTRACTION
METHYLENE CHLORIDE EXTRACTION
METHYLENE CHLORIDE EXTRACTION
HOMOGENIZE AND DIVIDE
PENTANE EXTRACTION IN SOXHLET, PLUS XAD-2 MODULE RINSES
PORTION FOR INORGANIC ANALYSIS
GC, C_1-C_6
1. GC, C_7-C_{12} 2. TOTAL SAMPLE -IR 3. LC FRACTIONATE SAMPLE - IR/LRMS
1. GC, C_7-C_{12} 2. TOTAL SAMPLE -IR 3. LC FRACTIONATE SAMPLE - IR/LRMS
1. TOTAL SAMPLE -IR 2. LC FRACTIONATED SAMPLE -IR/LRMS
1. TOTAL SAMPLE -IR 2. LC FRACTIONATED SAMPLE -IR/LRMS
1. GC, C_7-C_{12} 2. TOTAL SAMPLE -IR 3. LC FRACTIONATE SAMPLE - IR LRMS
1. TOTAL SAMPLE -IR 2. LC FRACTIONATED SAMPLE -IR/LRMS

Source: Reference 1.

FIGURE 1 ORIGINAL MULTIMEDIA OVERVIEW OF SAMPLES FOR ORGANIC ANALYSIS


ORGANIC ANALYSIS
GASES
LIQUIDS
SOLIDS
ON SITE G.C. FOR C1-C6 HYDROCARBONS
ORGANIC LIQUIDS
AQUEOUS SOLUTIONS
SOLID MATERIALS
PARTICULATE OR ASH
XAD-2 SORBENT TRAP
G.C., ALIQUOT FOR C1-C12 HYDRO-CARBONS
SASS TRAIN RINSES
SOLVENT EXTRACTION
INFRARED ANALYSIS
G.C., ALIQUOT FOR HYDRO-CARBONS TO C12
CONCENTRATE ALIQUOT FOR GRAVIMETRIC AND IR
CONCENTRATE ALIQUOT (8 - 600 mg)
LIQUID CHROMATOGRAPHIC SEPARATION
EIGHT FRACTIONS: WEIGHT
INFRARED ANALYSIS
LOW RESOLUTION MASS SPECTRA ANALYSIS*

*ON FRACTIONS EXCEEDING THRESHOLD CRITERIA

Source: Reference 1.

FIGURE 2 ORIGINAL LEVEL 1 ORGANIC ANALYSIS FLOW SCHEME

II. FIELD GC ANALYSIS OF ORGANIC GASES

The original Level 1 Procedures (1) recommended that organic gases (species with boiling points < 100°C) be collected in glass sampling bulbs and analyzed on-site by gas chromatography (Field GC procedure).

A. Sampling

Although the possibility of substituting polymeric plastic sampling bags was advocated, systematic studies (3) indicated that glass bulbs were the sampling system of choice for Level 1 purposes.

The instantaneous nature of gas grab samples with evacuated glass bulbs was of some concern. Experiments were performed to verify that a degree of time-integrated sampling with a previouly evacuated glass bulb can be achieved. If a glass fiber filter and an 0.2 Lpm critical flow orifice are used upstream, a 2 L bulb fills gradually over a 12-minute period after the stopcock is opened. The data are presented in Table 1 and Figure 3.

B. Analysis

The GC procedures listed in the June, 1976 Procedures Manual (1) for gas chromatographic analysis of sulfur gases and gaseous hydrocarbons were reviewed and found not to be satisfactory for Level 1 purposes. The revised procedures below were tested and recommended as replacements.

1. Sulfur Gases

Column:	36' x 1/8" Teflon^R, 12% polyphenylether and .5% H_3PO_4 on 40/60 mesh Chromosorb T (Note 1)
Detector:	Flame photometric (Note 2)

TABLE 1

RATE OF PRESSURE CHANGE OF PREVIOUSLY EVACUATED GLASS BULB FITTED WITH CRITICAL FLOW ORIFICE

Time (min)	Differential Pressure (mm)		
	Run 1	Run 2	Run 3
0	710	690	710
1	620	600	-
2	520	-	-
3	420	424	440
4	340	340	-
5	260	254	-
6	184	188	190
7	120	126	-
8	70	80	86
9	40	40	-
10	20	20	-
11	10	10	-
12	0	0	6

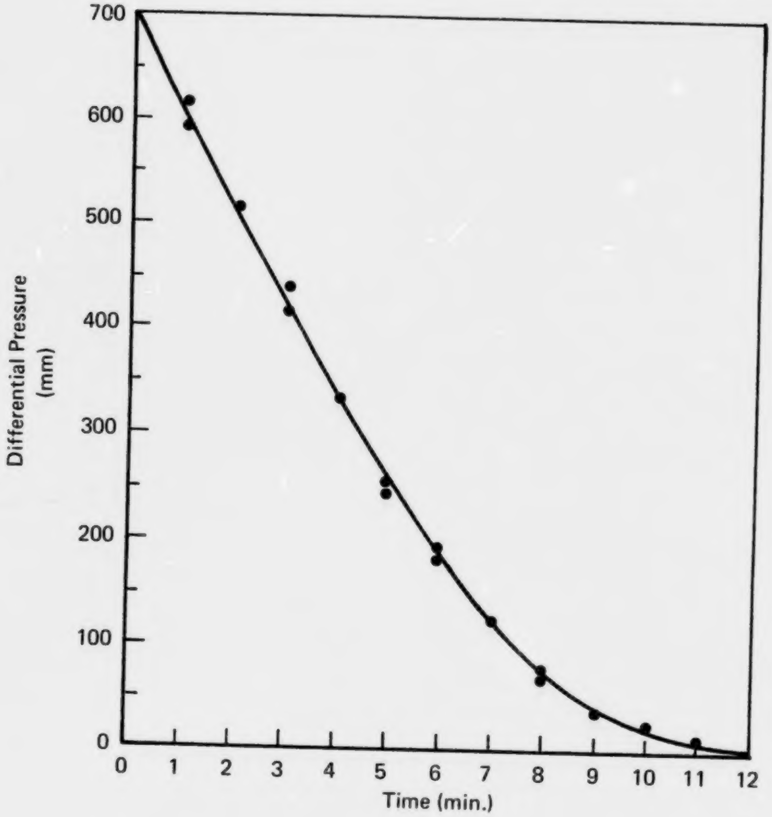


FIGURE 3 FILLING RATE OF PREVIOUSLY EVACUATED 2L GLASS BULB FITTED WITH 0.2 LPM CRITICAL FLOW ORIFICE

Conditions: Helium carrier at 30 mL/min.
Injector and detector temperatures: 110°C (Note 3)
Column oven temperature program:
isothermal at 60°C for 5 min.
increase at 10°min. to 100°C
hold at 100°C for 10 min.
(Note 4)

Notes:

1. Exit end of column should be fitted directly into the base of the detector, eliminating any metal transfer lines. On-column injection should be used.
2. The FPD response tends to saturate at concentrations greater than 2 ppm for a 10 mL injection volume. Injection should be repeated with smaller (1 or 0.1 mL) sample size if apparent concentration exceeds 2 ppm.
3. Detector temperatures above 130°C are reported to result in losses of sulfur species.
4. The conditions specified have been selected to give the following approximate retention times:

H_2S	3 min.
SO_2	4 min.
CH_3SH	6 min.
C_3H_7SH	10 min.

Slight modifications in the temperature and duration of the initial hold period may be necessary to accommodate variations in individual column performance.

2. Gaseous Hydrocarbons

The column choices and temperature programs specified in the June, 1976 manual for field GC of organic gases need to be modified because:

a. The "C_7-C_{12}" analysis was incorporated into an additional (TCO) procedure. (See Chapter VI)

b. A single GC analysis procedure could not be found that would cover the entire -160°C (methane) to 96°C (heptane) b.p. range.

In the new procedure, described below, the -160°C to 30°C b.p. range is analyzed using a temperature programmed run on Porapak Q. The 30°C to 100°C b.p. range is analyzed isothermally on 20% OV-101. Two separate GC procedures are required in order to allow resolution of the very volatile organics while eluting the higher boiling gases in a reasonable period of time. The GC systems will primarily be separating and analyzing mixtures of materials with given boiling point ranges, although the separations will also be influenced by polarity in some cases. A flame ionization detector is used.

The conditions recommended for these analyses are specified in Table 2. Slight modifications in temperature and duration of the isothermal hold periods and/or rate of temperature increases may be necessary to accomodate variations in individual column performance.

Figures 4 and 5 present example chromatograms for the low boiling and higher boiling calibration mixtures, respectively, under the recommended conditions.

Mixtures of normal hydrocarbons are used to calibrate the field GC procedures. A retention time vs boiling point calibration curve is prepared for each procedure in the standard manner. The Level 1 boiling point ranges and the hydrocarbons falling in each range are:

Level 1 Designation	B.p. Range (°C)	Hydrocarbon	B.p. (°C)
GC1	-160 to -100	Methane, C_1	-161
GC2	-100 to -50	Ethane, C_2	-88
GC3	-50 to 0	Propane, C_3	-42
GC4	0 to 30	Butane, C_4	0
GC5	30 to 60	Pentane, C_5	36
GC6	60 to 90	Hexane, C_6	69
GC7	90 to 100	Heptane, C_7	96

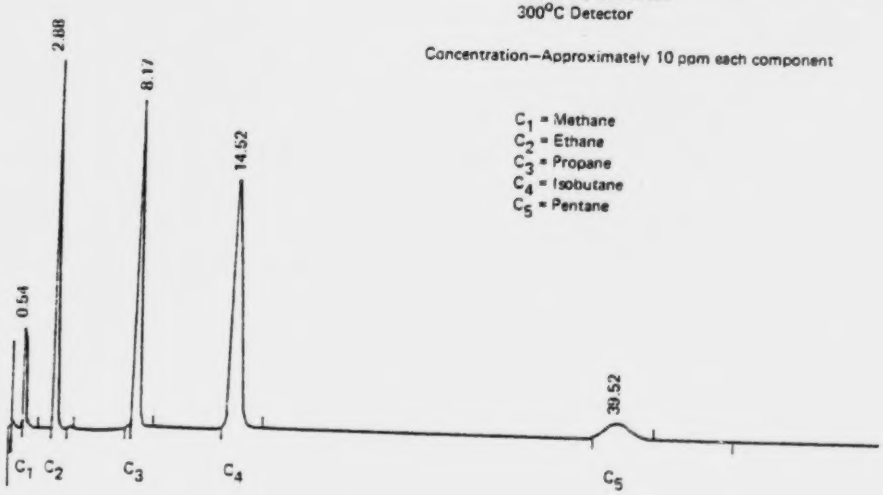
TABLE 2

RECOMMENDED PROCEDURES FOR FIELD GC OF ORGANIC GASES

B.p. Range	Column	Temperature and Conditions	Calibration Mixture
-160°C to 30°C (GC1 to GC 4)	2 m x 2 mm (6' x 1/6") Stainless Steel, Porapak Q	Helium carrier at 20 mL/min Injector and Detector temperatures: 200°C. Column oven temperature program: isothermal at 60° for 4 min; increase at 20°/min to 110°; hold at 110°.* Bake-out at 170°C as necessary between injections.	10 ppm (v/v) each of: methane ethane propane n-butane n-pentane
30°C to 100°C (GC5 to GC7)	2 m x 2 mm (6' x 1/8") Stainless Steel, 20% OV-101 on 100/120 mesh Chromosorb W-HP	Helium carrier at 20 mL/min Injector and Detector temperatures: 200°C. Column oven temperature: isothermal at 30°C.**	10 ppm (v/v) each of: n-butane n-pentane n-hexane n-heptane

* Under these conditions the approximate retention times of the n-hydrocarbons are: C_1, 1 min; C_2, 3 min; C_3, 8 min; C_4, 15 min; C_5, 40 min.

** Under these conditions the approximate retention times of the n-hydrocarbons are: C_4, 1 min; C_5, 2 min; C_6, 5 min; C_7, 12 min.



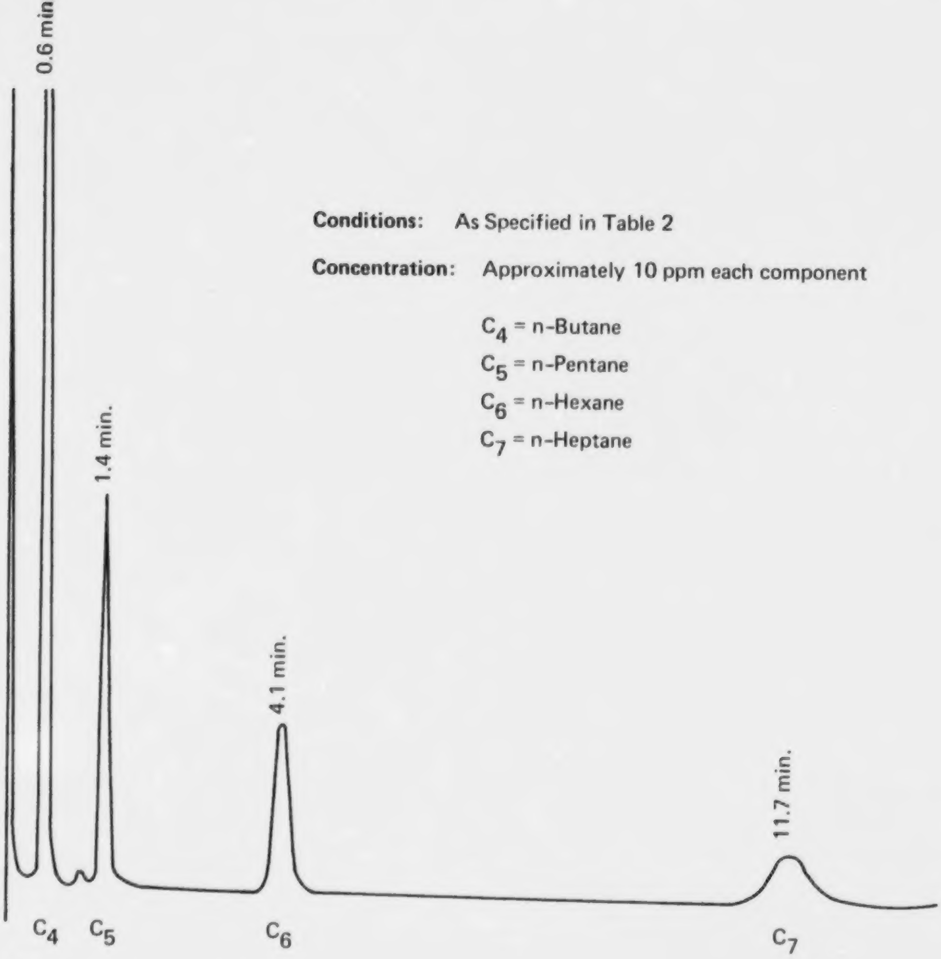
Conditions—60° C for 4 minutes than program to 110° @ 16°/min.
250°C Injection Port
300°C Detector

Concentration—Approximately 10 ppm each component

C_1 = Methane
C_2 = Ethane
C_3 = Propane
C_4 = Isobutane
C_5 = Pentane

Source: Courtesy of Raymond Merrill, PMB–EPA–RTP

FIGURE 4 GC OF −160°C TO 30°C B.P. RANGE ORGANIC GASES



Conditions: As Specified in Table 2

Concentration: Approximately 10 ppm each component

C_4 = n-Butane
C_5 = n-Pentane
C_6 = n-Hexane
C_7 = n-Heptane

Source: Arthur D. Little, Inc.

FIGURE 5 GC OF 30°C TO 100°C B.P. RANGE ORGANIC GASES

The GC systems should also be calibrated for quantitative analysis with the normal hydrocarbon mixtures. Assumption of uniform FID response for varying compound classes is acceptable in Level 1 analysis.

Since the chromatogram peaks for Level 1 samples will usually represent mixtures of materials present in a certain boiling range, rather than pure individual compounds, it is recommended that the chromatographic data be reported as follows:

Level 1 Designation	mg/m^3	No. of Peaks Observed
GC1		
GC2		
GC3		
GC4		
GC5		
GC6		
GC7		

It is important to recognize that in many, if not most, cases, the species present will not, in fact, be identical to those used for calibration of the on-site procedure.

III. PREPARATION AND CHARACTERIZATION OF XAD-2 RESIN

A macroreticular crosslinked polystyrene resin, XAD-2, was selected for use in the SASS train organic vapor sampling module (1) because of its high collection efficiency for a variety of organic compounds. The optimum procedures for preparation (clean-up) and analysis of the blank for XAD-2 resin were not specified in the June, 1976 manual.

A. Clean-up Procedures

The Procedures Manual for cleaning XAD-2 called for sequential extraction with water, methanol, ether and pentane. It was felt desirable to change the extraction sequence to one of water, methanol and methylene chloride for several reasons: there are some hazards associated with reflux of diethyl ether; a three-step sequence would be time saving; use of methylene chloride would result in one common solvent for all of the organic extracts; and the solubility of many compounds is better in methylene chloride than pentane.

Two different 3-step conditioning procedures (water + methanol + pentane and water + methanol + methylene chloride) were compared to the original 4-step procedure (water + methanol + diethyl ether + pentane). Parameters investigated include the surface properties of resin (pore volume and pore size distribution) and the quantity and nature of residual solvent extractable material. Further experiments examined the possibility of resin self-contamination by thermal processes (at 20°, 40° and 60°C) and the efficiency of recovery of spiked materials.

Based on these studies, the new recommended procedure is to clean the XAD-2 resin with the water, methanol, methylene chloride overnight extraction sequence and to extract the collected SASS sample with methylene chloride.

Several batches of XAD-2 were prepared by the solvent sequence described above. All batches appeared to behave similarly based upon general observations. In order to determine whether there was any difference between the old extraction sequence (pentane finish) and the new sequence (methylene chloride finish), compound elution behavior, surface areas, and residual blank levels were examined.

The elution volumes, V_g(mL/g), were compared for XAD-2 prepared by the two routes by testing with phenol, octane and benzene. The results are shown in Table 3. There was no difference in V_g between the batches of resin prepared by the two techniques, within experimental error.

Surface areas of the XAD-2 prepared by the two methods were:

Final Solvent	Surface Area (m^2/g)	Pore Volume (cc/g)
Pentane	366	0.891
Methylene Chloride	376	0.886

To compare residual (blank) contaminant levels, 20 g samples of XAD-2 prepared by each method were extracted with both pentane and methylene chloride. Half of the extract from each sample was taken to dryness for gravimetric analysis. Thus the residue data obtained represented that derived from 10 g of XAD-2 or about 7% of the amount of XAD-2 in a SASS module. The results obtained were as follows (mg):

	Pentane Extract	Methylene Chloride Extract
Pentane Clean	0.0	0.6
Methylene Chloride Clean	0.0	0.1

The data showed that acceptable levels of residue were obtained by both methods. If the differences were taken to be significant, then it would appear that methylene chloride did a better initial job in cleaning the XAD-2 resin.

TABLE 3

ELUTION VOLUMES OF XAD-2 PREPARED BY TWO METHODS

Challenge Compound \ Solvent**	V_g (mL/g)* at Temp. 96°C		135°C	
	C_5H_{12}	CH_2Cl_2	C_5H_{12}	CH_2Cl_2
Phenol	4230	4250	382	386
Octane	2390	2400	215	211
Benzene	--	--	47	41

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[*] Vg is the volume of gaseous sample that can be passed over a 1 g sorbent bed in a frontal chromatography experiment before the exit concentration of organic compound exceeds 50% of the challenge concentration.

[**] Final solvent in clean up.

Details of a revised clean-up procedure, including a quality control check to verify acceptable blank levels of extractable material, are given in Appendix B.

B. Blank Determination

A series of experiments were conducted in an effort to quantify and characterize the material that might result as a blank on XAD-2 sorbent traps. These experiments were done at one-fifth scale compared to the SASS Level 1 Procedure. A glass sorbent trap was used; this trap has the same sorbent bed depth as the SASS sorbent module but is smaller in diameter. The glass trap held 41.±1. g of XAD-2 resin, previously cleaned by sequential extraction with water, methanol, diethyl ether, and pentane.

A clean gas stream was generated by drawing nitrogen gas from a cylinder of liquid nitrogen. The gas stream temperature was controlled at 20, 40 or 60°C by passing the gas through a 182 cm (6') x 12.5 cm (0.5") diameter heated glass-lined probe immediately upstream of the XAD-2 trap. The trap itself was jacketed with a heating mantel. Temperatures were monitored by thermocouples at the probe exit and at the outer surface of the sorbent trap.

A Research Appliance Corporation Staksampler^R control module was used to control the nitrogen flow rate and to measure the total volume of nitrogen passed through the trap. The measured volume was 6.53 ± 0.03 standard cubic meters (230.7 ± 0.9 standard cubic feet).

After exposure of the traps to the nitrogen stream, the XAD-2 resin was transferred to pre-extracted Soxhlet thimbles and extracted for 24 hours with methylene chloride. Each extract was transferred to a 250 mL volumetric flask and made to volume with additional methylene chloride. The weight of material extracted was determined by evaporation of 150 mL of the extract to dryness in a tared container at ambient conditions.

	Found mg/150 mL of Extract	Calculated mg/trap
20° Trap	2.985	4.98
40° Trap	1.731	2.88
60° Trap	1.628	2.72

The quantities of material found were only somewhat higher than the 1-2 mg amounts that have routinely been found on evaporation of 200 mL of solvent. The quantities found for the traps exposed to nitrogen at elevated temperature were not significantly higher than the 1.5 - 3.8 mg amounts that had been found in previous work for unexposed (40 g) traps extracted with pentane and methanol.

The residue from the 150 mL of extract was mixed with a small quantity of silica gel and transferred to the top of a silica gel column prepared according to the Level 1 LC procedures. A four fraction separation was performed using the sequence of solvents shown below:

Fraction No.	Elution Solvent
1	20 mL pentane
2	10 mL methylene chloride
3	10 mL 50% methanol in methylene chloride
4	10 mL of 70-30-5: methanol, methylene chloride, conc HCl.

A control column, to which no sample was added, was run in parallel with the samples.

In this 4-fraction LC procedure, fraction 1 contains the aliphatic hydrocarbons, fraction 2 the aromatics, fraction 3 the polar (oxygenated) material and fraction 4 any very polar compounds (carboxylic acids). The aromatic fraction was investigated most thoroughly because it was expected that any decomposition products of the styrene-divinyl benzene resin would be aromatic compounds.

Quantitative gas chromatographic analysis was done both on the unconcentrated initial total extracts and on the aromatic fractions from the LC separation. The resulting estimates of total quantities of material with boiling points lower than about 320°C were:

	mg/trap (40 g XAD-2)	
	Unconcentrated Extract	Aromatic Fraction
20° Trap	≤0.8	≤0.000
40° Trap	≤0.4	≤0.004
60° Trap	≤0.5	≤0.002
Control LC Column (no sample)	(NA)	≤0.003

A 1 mL aliquot of the aromatic fraction from the 40° trap LC separation was evaporated to dryness in a tared aluminum pan. After evaporation of solvent, no change in pan weight was found; the quantity of non-volatile material was therefore <0.1 mg mL or <1 mg/trap for this sample. (At the time the gravimetric determination was done there was not sufficient sample remaining from the 20° and 60° trap aromatic fractions, so no GRAV data were acquired on those samples.)

The IR spectra of residues obtained by evaporation of 2 mL of the aromatic fractions of the three samples and of the control column (no sample) showed:

Assignment	Frequency	Intensity
NH or OH	(3200 - 3600 cm^{-1})	(m)
C=O ester	(1740 cm^{-1})	(w)
C=C	(1640 cm^{-1})	(w)
aliphatic CH_2, CH_3	(2850 - 2950 cm^{-1})	(m-w)
silicate or phosphate	(1000 - 1100 cm^{-1})	(m)

The aliphatic CH_2, CH_3 bands were slightly stronger in the three trap samples than in the control, but the spectra were otherwise similar.

Examination of the aromatic fractions by LRMS, using the direct insertion probe led to the results shown in Table 4. Because the total signal intensity was found to be so low, a one mL sample (rather than the more usualy 100 µL) was dried down for the probe. The results in Table 4 indicate that the major aromatic species produced by exposure of XAD-2 to heated nitrogen gas were alkyl benzenes, small polymers of styrene, and fragments of polymers. The composition of the polymers and fragments was confirmed by HRMS peak matching of a number of peaks. Both the relative and the absolute quantities of stryrene-like polymers and fragments increased as the trap exposure temperature increased. The total amount of material that was volatile in the probe also increased. This indicates that some thermal decomposition or thermal desorption of entrained material is occurring and, in fact, the species found include the types of materials which would be expected to arise from decomposition of the styrene-divinyl benzene resin. The polymers and fragments appear in the LRMS at probe temperatures of about 150°C. The phthalates and polynuclear aromatic hydrocarbons found in roughly equal amounts in all four cases, including the aromatic fraction from the control column, are most probably contaminants introduced by the solvent, the silica gel or other sources.

In summary, the experiments reported here indicate that the only significant contaminants that can be expected as a sorbent trap "blank" due to thermal decomposition of the XAD-2, in the temperature range of 20-60°C, are small polymers and fragments of polymers that include 1 to 4 styrene units. These species would appear in the aromatic fraction(s) of the LC scheme and would be detected by the LRMS analysis. The quantity of material which these species represent is expected to be too small to detect by gravimetric analysis (i.e., <0.1 mg), although the apparent total "blank" --including solvent-introduced and other contaminants like silicones and phthalates--may be higher.

TABLE 4. SUMMARY OF LRMS RESULTS FOR AROMATIC FRACTIONS (LC FRACTION 2) OF SORBENT TRAP EXTRACTS

	Control Column (no sample)	20° Trap	40° Trap	60° Trap
Total LRMS signal intensity (arbitrary units) for 1 ml sample	1000	800	1700	3600
Distribution of Species:				
Polynuclear Aromatics (napthalene, anthracene, pyrene)	3%	13%	4%	3%
Phthalates	4%	8%	4%	2%
Alkyl benzenes, MW 91 and 105	3%	33%	15%	16%
Styrene Polymers and Fragments				
1 styrene unit		25%	38%	40%
2-4 styrene units		18%	22%	28%
Others	mw 112, 20%	mw 145, 3%	mw 129, 4%	mw 129
	129, 25%		145, 6%	145
			167, 2%	167

C. Wet vs. Dry Storage of Cleaned Resin

An experiment was carried out to ascertain the effect on cleaned XAD-2 resin of dry storage vs. storage under methanol vs. storage under methylene chloride until just prior to use.

A single lot of resin was cleaned according to Level 1 procedure using Burdick & Jackson solvents. The cleaned resin was divided into three portions: one was stored under methanol, the second was stored under methylene chloride, and the third was dried (at a later date) according to Level 1 procedure.

The three portions (dried, methanol storage, and methylene chloride storage) were extracted after allowing the dry material to stand 60 days and the two wet portions 90 days. The extracts were concentrated from 200 mL to 10 mL by K-D concentrators, and portions taken for TCO* and GRAV. Results are in Table 5.

The total blank levels measured for dry storage and for methylene chloride storage were about what one would expect for samples that have passed the Level 1 QC check (Appendix B). Considerably higher blank levels were found for XAD-2 stored under methanol.

These data indicate that wet storage under methanol is not the method of choice for XAD-2 to be used in Level 1 air sampling.

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*Total Chromatographable Organics. See Section VI B

TABLE 5

BLANK LEVELS FOR WET VS DRY STORAGE OF CLEANED XAD-2 RESIN

	TCO*	GRAV	TOTAL
Dried Resin	0.001 mg/g	0.044 mg/g	0.04 mg/g resin
MeOH Storage	0.024 mg/g	0.182 mg/g	0.21 mg/g resin
CH_2Cl_2 Storage	0.005 mg/g	0.030 mg/g	0.04 mg/g resin

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[*] Total Chromatographic Organics. See Section VI.

IV. EXTRACTION OF AQUEOUS SAMPLES

The June, 1976 Level 1 Procedures Manual (1) suggested that aqueous samples be adjusted to neutral pH and then sequentially extracted with three 500-mL portions of methylene chloride for a 10 liter water sample.

A literature study of the efficiency to be expected from methylene chloride solvent extraction of aqueous samples, based on octanol-water partition coefficients, was conducted. That study indicated that the original Level 1 procedure (1), which called for three extractions at neutral pH, was inadequate for Level 1 purposes, since moderately strong organic acids and bases would be <0.1% extracted.

The proposed revised procedure for Level 1 extractions was as follows:

> Extraction of aqueous solutions should be carried out with methylene chloride using a standard separatory funnel fitted with a Teflon stopcock. The pH should be adjusted to 2.0 ± 0.5 with hydrochloric acid, and then to 12.0 ± 0.5 with sodium hydroxide, using multirange pH paper for indication. Two extractions at each pH using 500 mL portions of methylene chloride for a 10 liter sample should be sufficient.
>
> (Extraction first at acid pH is recommended to reduce emulsion formation by removing some surfactants in their neutral form. If emulsions do occur, however, they can generally be broken by centrifugation due to the high density of chlorinated solvents.)

Neutral species, whose recovery is independent of pH, are essentially extracted four times by this procedure, while acidic and basic species are each extracted twice. The following shows the organic solvent/water partition coefficients necessary to achieve a specified % recovery by the modified, 2 pH, procedure:

Type of Species	Effective No. of Extractions	Necessary P_{org/H_2O} for 50% Recovery	75% Recovery
Neutral	4	3.8	8.3
Acidic, Basic	2	8.3	20.0

Table 6 presents estimated P_{org/H_2O} values for some species that are readily extractable and some that are essentially non-extractable, even by the revised procedure.

Partition coefficient data suggest that etner may be superior to methyllene chloride for extracting certain acidic compounds, such as phenols or carboxylic acids. This was tested experimentally to see if the advantage was significant. A stock solution of phenol, N-methyl aniline, acenaphthene,n-hexadecane and 4,4,'dichlorobiphenyl in methanol was spiked into samples of reagent grade water. Samples were made basic (pH ∿ 11) and extracted twice with 50 mL of methylene chloride, then made acidic to approximately pH 2. One was extracted twice with 50 mL of methylene chloride and the extract combined with that obtained at pH 11, while the other was extracted twice with 50 mL of ether and the extract combined with that obtained at pH 11.

The experimental data are presented in Table 7. Four of the five model compounds were extracted efficiently with either methylene chloride or ether. Phenol was extracted four times more efficiently by ether than by methylene chloride yielding an 82% recovery versus only a 20% recovery. In view of the inconvenience (lighter than water) and potential peroxide explosion hazard associated with ether use, the improvement in efficiency was considered to be only marginally important.

Since, furthermore, higher homologs of phenol such as cresols were adequately extractable with methylene chloride, the use of diethyl ether was not recommended for Level 1 purposes.

TABLE 6

ILLUSTRATIVE VALUES OF SOLVENTS: WATER PARTITION COEFFICIENTS*

Compound			
Efficiently Extracted	$P_{CHCl_3:H_2O}$	$P_{heptane:\ H_2O}$	$P_{ether:\ H_2O}$
Propyl Ether	580.	34.	18.
Hexyl Amine	490.	30.	16.
Butyl Mercaptan	1,200.	98.	34.
Benzene	460.	24.	15.
Chlorobenzene	6,200.	1,100.	150.
Indene	78,000.	1,500.	180.
Acridine	20,000.	9,300.	575.
Thiophene	301.	13.	10.
Inefficiently Extracted			
Acetic Acid	0.03	1.0	0.4
Phenol	2.	0.05	31.
Benzene Sulfonic Acid	0.0001	0.000006	0.002
Ethylene Glycol	0.002	0.00001	0.005

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* Estimated using data base and methods of Reference 5.

TABLE 7

RELATIVE RECOVERIES OF VARIOUS COMPOUNDS AFTER EXTRACTION FROM WATER*

Model Compound	% Recovery Methylene Chloride	% Recovery Methylene Chloride -Ether	Ratio Methylene Chloride-Ether to Methylene Chloride
Phenol	20	82	4.0
N-methylaniline	95	108	1.1
Acenaphthene	95	99	1.04
n-hexadecane	94	100	1.06
4,4' Dichloro-biphenyl	95	100	1.05

* Each number is the average of two analyses.

V. EXTRACTION OF SLUDGE/SLURRY SAMPLES

The June, 1976 Procedures manual (1) included no explicit Level 1 procedure for preparation of sludge/slurry samples prior to organic analysis. This sample category can span a tremendous range, including slurries and solids or semisolid sludges containing up to 95% water. Some of these materials are very difficult to handle and no one procedure will work for all of them. Nevertheless, it was desirable to define a sample preparation protocol that could be applied consistently and that would minimize variability. The following protocol was tested using a variety of complex sludge/slurry samples that had been acquired in other programs.

The basic approach is to determine whether the sample is best treated as a solid, a liquid, or by a combination of procedures. The protocol will involve, in most cases, tests on small portions of the 1 Kg sample to determine the best procedure prior to committing the entire sample. The stepwise protocol is:

- If the physical character of the sample permits, treat it as a solid. That is, transfer the whole sample to a Soxhlet thimble and extract for 24 hrs with methylene chloride. Do not dry sample before extracting. Determine wet weight of sample taken by weighing sample container before and after transferring sample to thimble. If an aqueous phase is noticed in the organic extract, this should be separated and removed prior to concentration.

- If the sample state does not appear compatible with direct Soxhlet extraction (i.e., wet sludge/slurry of high liquid content) select a treatment procedure as follows:

  - Take a 10 mL portion of the sample (shaking vigorously first, if necessary, to facilitate a fairly representative sampling) and place in a 15 mL centrifuge tube. Add 2 mL methylene chloride. Shake well and allow to settle for at least 30 min. Then:

If sample dissolves completely, treat the sample like a neat organic liquid--no sample preparation is required.

If a clean two-phase (organic-aqueous) separation is achieved, treat the sample like an aqueous sample.

If a clean two-phase separation is not achieved (i.e., if an emulsion forms, or if the apparent solvent recovery is low, or if a three-phase system with solids suspended in organic layer or between organic and aqueous layers is present), centrifuge the mixture. If a clean two-phase system then results, treat sample as indicated above. If not, test sample as suggested below.

Take a 10 mL portion of the sample (shaking vigorously first, if necessary, to facilitate a fairly representative sampling) and place in a 15 mL centrifuge tube. Centrifuge. If phases separate, treat the solid phase by Soxhlet extraction. The liquid phase is treated like an aqueous sample,or, if organic, like a neat organic liquid. The several extracts generated for this type of sample should be recombined--taking the same fraction of each--prior to organic analysis.

This protocol was evaluated using two fairly intractable samples--one sludge and one slurry--acquired in the course of other programs. The protocol was found to be generally satisfactory for those samples. It was also found that when difficult-to-break emulsions are encountered, the most effective and convenient strategies for breaking them are (in decreasing order of preference):

centrifugation
addition of more organic solvent
freezing.

VI. ANALYSES OF VOLATILE SPECIES IN ORGANIC EXTRACTS: TCO AND SOLVENT EXCHANGE

A. Problem Definition

The original Level 1 Organic Analysis Procedure, as specified in the June 1976 Procedures Manual (1), was designed in a manner which provided qualitative compound class identification and quantitative (gravimetric) data for those components of a sample that are retained when an organic sample extract is evaporated to dryness.* It was implicitly assumed that all compounds with boiling points ≥ ca. 220°C (C_{13} and higher normal hydrocarbon range) would be retained and carried through the LC-IR-LRMS procedure, while those boiling below 220°C (C_{12} and lower normal hydrocarbons down to C_7*) might be lost to varying extents during sample evaporation to dryness.

Quite early in the experimental investigation of the LC-IR-LRMS organic analysis procedure, it became apparent that the range of material lost when the sample extract was evaporated to dryness for the gravimetric analysis and preparation of the LC sample was considerably higher than expected. Data were obtained (Table 8) which suggest that most compounds in the <216°C boiling point range will be completely lost if a sample extract is evaporated to constant weight (several hours or more of drying). Quantitative retention of the model compounds appeared to be achievable only for species with boiling points of about 300°C and above. At about the same time, it was recognized that many, if not most, of the organic compounds that were considered to be of primary concern in Environmental Assessment [for example, the compounds on the multimedia Environmental Goals (MEG) list (6)], were in the <300°C boiling point range that would

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*A gas chromatographic procedure had been incorporated in the procedures (1) to provide some quantitative information (quantities of material in defined boiling point ranges) on the "C_8 to C_{12}" range species. Very volatile organics, with boiling points below about 100°C, including the C_6 and lower hydrocarbons, were to be analyzed by on-site chromatography.

TABLE 8

RATE OF EVAPORATION OF MODEL COMPOUNDS*

Compound	B.P.	mg Taken	% Loss/ Time Interval
Tetrachloroethane	146°	111	52%/15m; 88%/35m
Cumene	152°	98	79%/12m; 99%/30m
n-Decane	174°	--	89%/60m
Benzaldehyde	180°	100	6%/10m; 21%/30m
Phenol	182°	105	6%/45m; 11%/80m
2-Ethyl-1-hexanol	184°	113	10%/30m; 23%/70m
N-Methyl aniline	196°	104	11%/30m; 25%/70m
n-Dodecane	216°	70	12%/60m
O-Nitrotoluene	220°	115	7%/85m
Dihexyl ether	223°	104	15%/85m
Diethyl phthalate	296°	128	0%/85m

*Sample pipetted into tared aluminum pan and allowed to stand uncovered at room temperature.

correspond to loss prior to LC. Thus, no compound class information would be available from Level 1 methods as originally published, to indicate the possible presence of significant amounts of these materials. It was considered desirable to modify the Level 1 procedures to improve the qualitative information obtainable for organics boiling below about 300°C.

Preliminary studies indicated that the dramatic loss of moderately volatile material occurs only after the sample has been evaporated to dryness. Concentration of an extract by a factor of 10 to 100 (1 mL or 0.1 mL final volume from 10 mL extract) produces less drastic losses (Table 9). Figure 6 illustrates comparable results of a second series of concentration and recovery experiments. Quantitative recovery, after concentration of pentane extracts to 100 μL, was achievable only for test species with boiling points over 300°C. Other data showed that recoveries similar to those in Figure 6 could be achieved when a 10 mL aliquot of pentane solution was evaporated to dryness after addition of 200 mg of silica gel.

T9

F6

At one point it was suggested that the presence of high molecular weight materials, which are frequently found in extracts from real environmental samples, might aid in retaining volatile materials when the extract is evaporated to dryness. A brief experimental check of this possibility was undertaken using phenol (b.p. 182°C) as a model volatile organic compound. "Extracts" were prepared by dissolving 20 mg of phenol and 50 or 100 mg of previously dried high molecular weight organic waste in 10 mL of methylene chloride. These solutions were washed into tared pans and dried to constant weight. Results (Table 10) implied that phenol recoveries were no higher in the presence of complex organic matrices, since the weight loss in each case corresponded approximately to the quantity of phenol present in the extract.

T10

It was decided to modify the procedures for preparation of sample extracts prior to LC to avoid evaporating the sample to dryness and thus allow acquisition of some qualitative chemical information about species in

TABLE 9

EFFECT OF CONCENTRATION OF PENTANE EXTRACTS ON LOSS OF MODEL COMPOUNDS

Compound	B.P., °C	% Recovery After Concentration to: 1 mL	100 μL
C_7 n-heptane	96	78	45
C_8 n-octane	117	86	53
C_9 n-nonane	151	88	52
C_{10} n-decane	174	89	56
C_{11} n-undecane	196	88	52
C_{12} n-Dodecane	216	89	53
Cumene	152	89	31
Benzaldehyde	180	86	53

10 mL samples concentrated to 1.0 mL or 0.1 mL at room temperature under a nitrogen stream. Original concentration ∿50 ppm.

Volume restored to 10 mL and samples analyzed by GC.

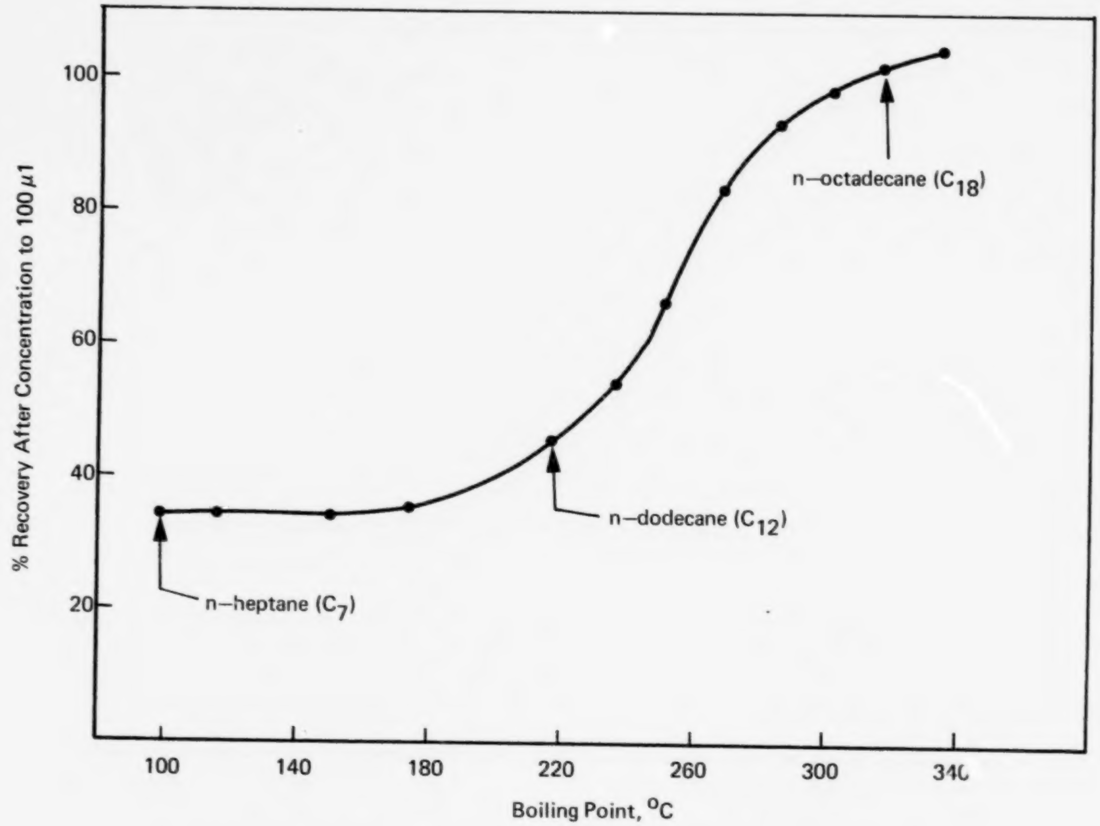


FIGURE 6 RECOVERIES OF N–HYDROCARBONS VS. BOILING POINT AFTER CONCENTRATION OF PENTANE SOLUTIONS

TABLE 10

RECOVERY OF PHENOL AFTER DRYING SOLVENT EXTRACTS CONTAINING HIGH MOLECULAR WEIGHT ORGANICS

	mg		
	Taken*	Recovered**	Lost
20 mg Phenol	20	--	20.0
20 mg Phenol + 50 mg Waste I	70	47.1	22.9
20 mg Phenol + 100 mg Waste I	120	93.9	26.1
20 mg Phenol	20	20	20.0
20 mg Phenol + 100 mg Waste II	121	102	19.0
		Average Loss	22 mg
		Standard Deviation	3 mg

---

* Total mg of organic material dissolved in pentane.

** Residue remaining after evaporation to constant weight (± 0.1 mg).

the <300°C boiling point range. It was also necessary to specify an alternative procedure for quantitative analysis of materials in the 100-300 °C range.

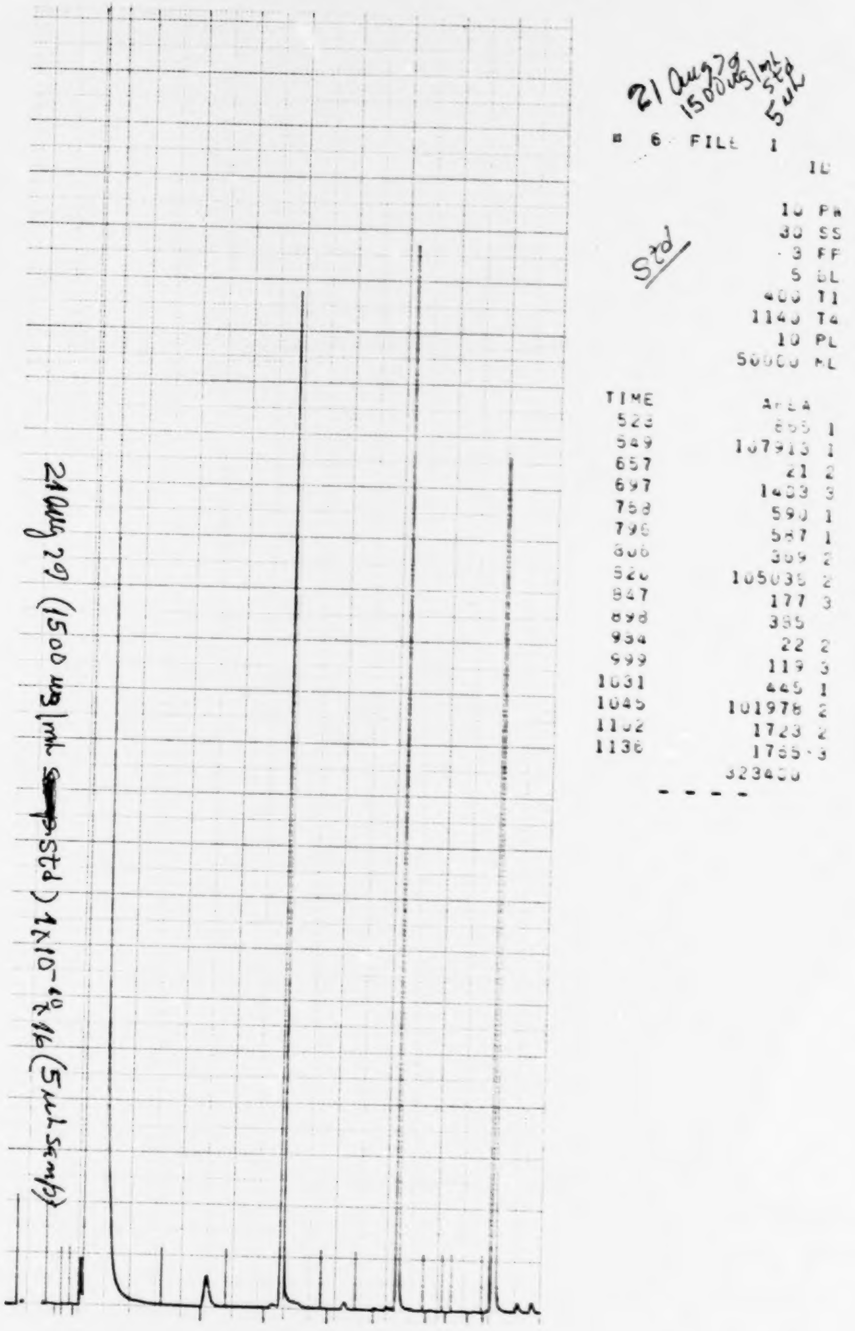
B. Quantitative Analysis of Volatiles: TCO

A procedure based on gas chromatography with a flame ionization detector was investigated as a method of quantitative analysis of extracted organic materials in the 100°-300°C boiling point range. The approach taken was to select a GC column and temperature program conditions that would: (a) adequately resolve species with 100°C boiling point from the solvent peak and (b) allow elution of species with 300°C boiling point in a reasonable period of time. No importance was placed on resolution of peaks eluting within the desired range (corresponding to 100-300°C boiling point); the objective was to obtain a single estimate of the quantity of volatile material, analogous to the "mg" value achieved by gravimetric quantification of non-volatile species in the extract.

A satisfactory column for this Total Chromatographable Organics, or TCO,* was found to be 1.8 m x 3 mm O.D. (6' x 1/8") 10% OV-101 on 100/120 mesh Supelcoport. The GC was operated isothermally at about 30°C--or room temperature--for five minutes after sample injection and then programmed rapidly to 250°C and held as long as necessary. Figure 7 shows a typical chromatogram for TCO analysis of standards composed of pure normal hydrocarbons. Figure 8 shows a chromatogram for TCO analysis of an environmental sample extract. Figure 9 presents a calibration curve for TCO, based on automatic integration of the FID signals over a retention time window defined by the C_7 and C_{17} n-hydrocarbons.

---

*The acronym originally proposed was GCMA, for Gas Chromatographic Mass Analysis. This was discarded to avoid confusion with GC/MS. An alternative to TCO may be required to avoid confusion with TOC.



21 Aug 79 1500 ug/ml Std 5 ul

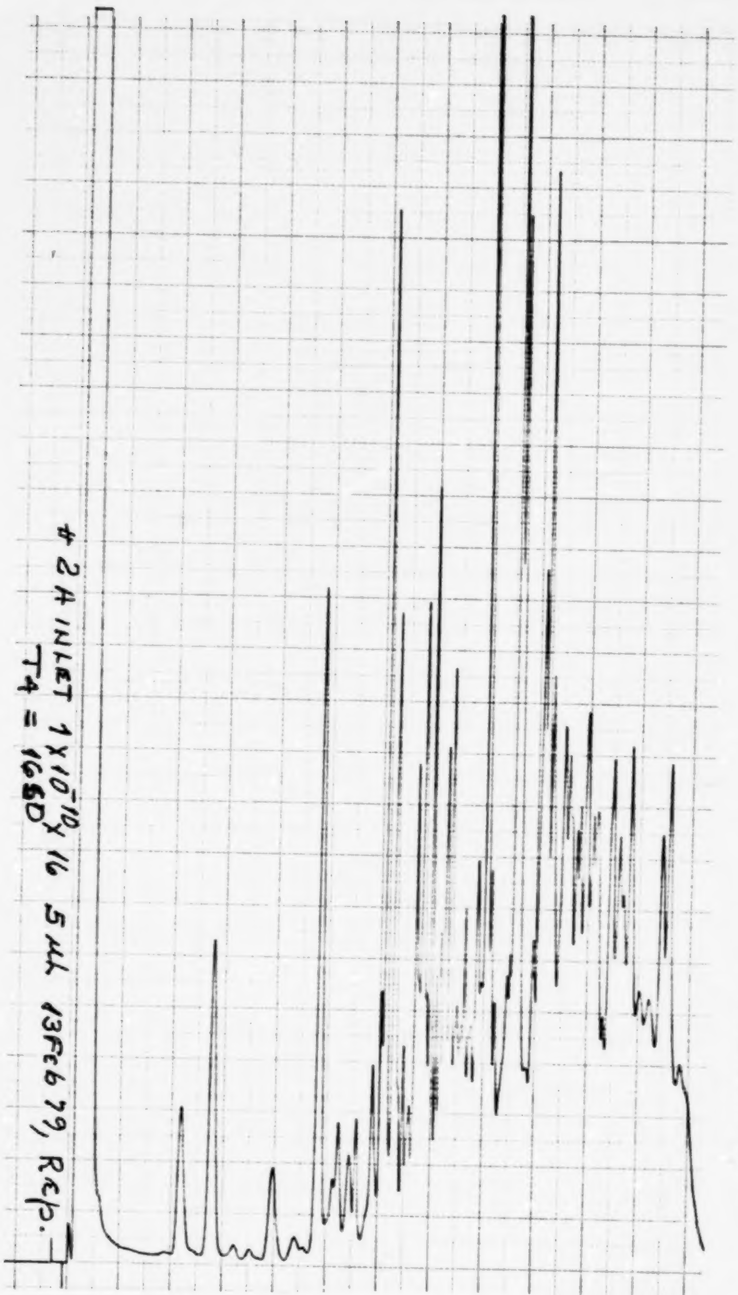
Std

```
■ 6 FILE 1
                    ID

                 10 PW
                 30 SS
                  3 FF
                  5 BL
                400 T1
               1140 T4
                 10 PL
              50000 ML

TIME             AREA
 523              855 1
 549           107913 1
 657               21 2
 697             1403 3
 758              590 1
 796              587 1
 806              309 2
 820           105035 2
 847              177 3
 898              385
 934               22 2
 999              119 3
1031              445 1
1045           101978 2
1102             1723 2
1136             1755 3
               323400
     - - - -
```

21 Aug 79 (1500 ug/ml std) 1x10^-10 x 16 (5 ul samp)

21 August, 1979 (1500 μg/mL std.) 1×10^{-10} x 16 (5μL samp)

FIGURE 7 TCO CHROMATOGRAM FOR C_8, C_{12} AND C_{16} QUANTITATIVE CALIBRATION MIXTURE



```
#10                  ID
                  10 P#
                  30 SS
                   5 BL
                  60 TP
                 400 T1
                1650 T4
TIME            AREA
 418          165862 6
 472           16860 6
 508           17462 6
 561           51839 1
 613           14018 .1
 632            5043 1
 666          262700 1
 700           36094 1
 712           51664 1
 737           47065 1
 753           42742 1
 791           90856 1
 819          313714 1
 841          231263 1
 861           46012 1
 875           55560 1
 888          151266 1
 905          240508 1
 925          189336 1
 937           61630 1
 946           70970 1
 957          131076 1
 969          142738 1
 983          104182 1
1002          131720 1
1015           94659 1
1029          133662 1
1049          415223 1
1060           69787 1
1070           68595 1
1099          179785 1

Total         3657931
```

2A Inlet $1 \times 10^{-10} \times 16$ 5µL 13 February, 1979, Rep.
T_4 = 1650

FIGURE 8 TCO CHROMATOGRAM FOR AQUEOUS SAMPLE EXTRACT

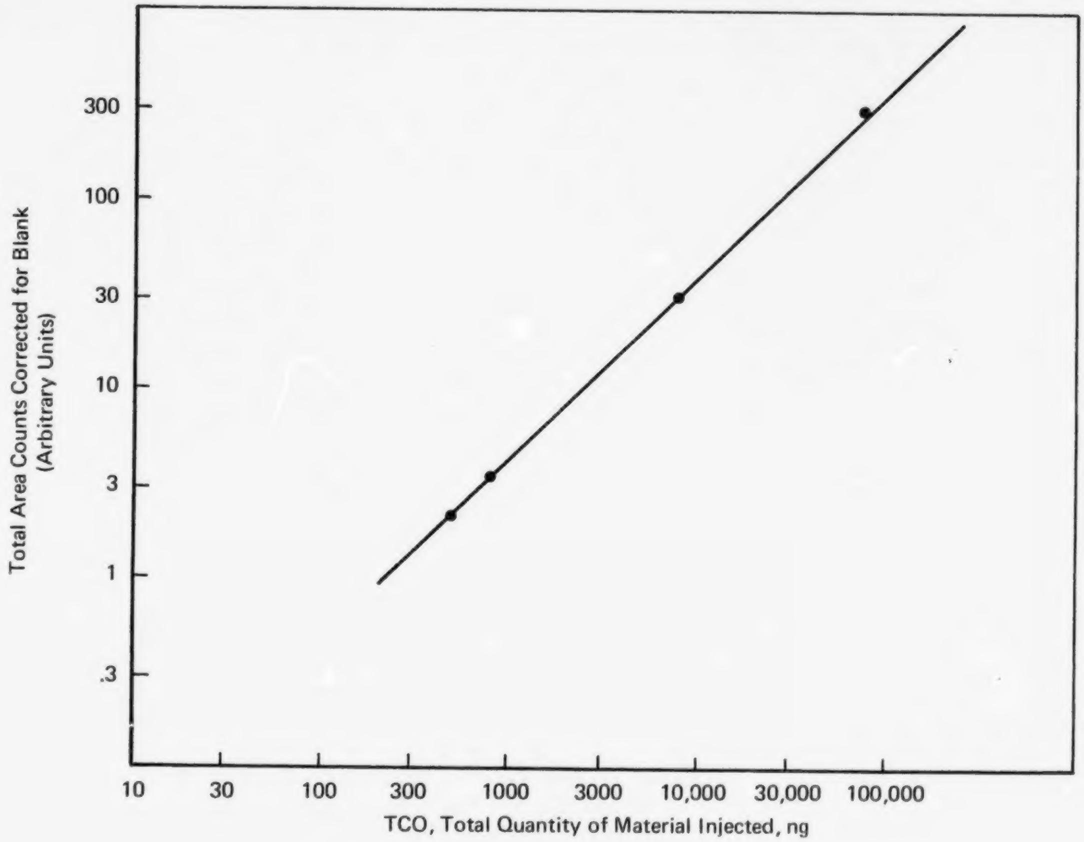


FIGURE 9 EXAMPLE CALIBRATION CURVE FOR LEVEL 1 TCO ANALYSIS

From the calibration curve and the total integrated area of the GC trace in Figure 8, the TCO of the example environmental sample extract is estimated to be 350 mg of volatile organics.

C. Sample Preparation for Extracts Prior to LC

The data presented in Part A. above, showed that it would be necessary to modify the Level 1 procedures, to avoid evaporating the extract to dryness, in order to obtain some qualitative information about organics in the TCO range (100-300°C boiling point). On the other hand, it was necessary to eliminate the methylene chloride from the sample prior to the LC step, since it would alter the desired elution pattern. The feasibility of a solvent exchange procedure was, therefore, explored.

Table 11 presents some data for recovery of a number of model compounds that were subjected to a two-stage solvent exchange procedure. A 100 mL portion of methylene chloride solution containing the indicated compounds at known (ppm) concentrations was concentrated to 10 mL. This concentrated solution was added to 200 mg of silica gel in a graduated container, and the volume was reduced to 1 mL. One mL of the exchange solvent (hexane or cyclopentane) was added, and the mixture concentrated to 1 mL again. A second 1 mL portion of exchange solvent was added, and the mixture reconcentrated to 1 mL. Recoveries of the model compounds were determined by gas chromatographic analysis. Cyclopentane gave measurably higher recoveries than hexane and was, therefore, the exchange solvent of choice.

After a two-step solvent exchange, an estimated 14-20% of methylene chloride remained. One volatile and one relatively non-volatile aromatic hydrocarbon were selected for use as indicators of the effect that traces of methylene chloride have on the LC separation. The compounds chosen were cumene and acenaphthene.

TABLE 11

RECOVERIES OF MODEL COMPOUNDS AFTER SOLVENT EXCHANGE WITH HEXANE AND CYCLOPENTANE

Compound	B.P., °C	% Recovery*	
		Hexane	Cyclopentane
n-Hydrocarbons			
n-Heptane	96	5,5*	13,11*
n-Octane	126	25,32	47 44
n-Nonane	151	42,54	71,61
n-Decane	174	55,64	85,77
n-Undecane	195	65,72	88,83
n-Tridecane	243	82,89	93,94
n-Pentadecane	270	91,93	95,97
n-Heptadecane	303	91,88	92,92
Others			
Tetrachloroethane	146	48	95,100
Cumene	152	55,43	70,80
Benzaldehyde	180	60	70,80
Phenol	182		58,30
2-Ethyl Hexanol	185	74	78,80
N-Methylaniline	196		35,55
o-Nitrotoluene	220	75	85,85
Dihexylether	223	88	100,100
Quinoline	237	65	54,56
Acenaphthene	278	88,95	95,90
p,p'-Dichlorobiphenyl	316	98,103	101,100

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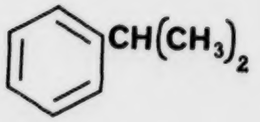
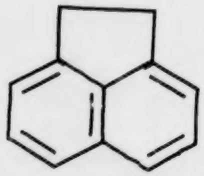
* Where two numbers are given, they represent results of replicate experiments.

Cumene



Acenaphthene



One mL samples of these compounds in cyclopentane solution containing know amounts of methylene chloride were put through the LC scheme.

The parameter of primary interest in these experiments was the percentage of the aromatic compounds that was found in fraction 1 (which is supposed to contain only aliphatic hydrocarbons) relative to the total amount recovered in fractions 1-4. The results in Table 12 indicate that the percent breakthrough of aromatics into fraction 1 is roughly equal to the percentage of methylene chloride in the sample applied to the column.

It seems that 10% breakthrough represents the upper limit of acceptability. It was decided to aim for a 5% or lower level of methylene chloride remaining in the sample after completion of the solvent exchange.

Subsequent experiments showed that a three step solvent exchange with cyclopentane gave 4-6% residues of methylene cloride without markedly increasing the losses of volatile materials. The three step exchange was done in two ways:

A. The methylene chloride solution was evaporated to 5 mL, then 5 mL of cyclopentane added. The mixture was then concentrated to 1 mL and 2 successive exchanges, each with 1 mL of cyclopentane, were carried out. This procedure does not increase the number of times the sample is reduced to 1 mL total volume.

B. The methylene chloride solution was evaporated to 1 mL. Three successive exchanges, each with 1 mL of cyclopentane, were carried out.

TABLE 12

BREAKTHROUGH OF AROMATICS INTO LC FRACTION 1

% Methylene Chloride in Cyclopentane	% Recovery in Fraction 1		
	Cumene	Acenapthene	Average
20	27	11	19
15	11	18	15
10	3	14	9
5	3	8	6

The recoveries are shown in Table 13, along with data obtained for a two step cyclopentane exchange done at the same time. The Table 13 data imply that recoveries from a three step exchange are not significantly lower than those from a two step exchange with the same solvent. (No plausible explanation, other than operator variability, has been found for the fact that the two step exchange experiment of Table 13 gave generally lower recoveries than the analogous experiment of Table 11.)

The three step exchange was therefore recommended for Level 1 LC of all sample extracts, except those *known* or *shown* to contain no TCO range material. In the latter case, evaporation to dryness prior to LC was recommended.

TABLE 13

RECOVERIES OF MODEL COMPOUNDS AFTER SOLVENT EXCHANGE

Compound	% Recovery 2-Step Exchange	3-Step Exchange a*	 b*
Tetrachloroethane	58	52	45
Cumene	60	54	43
Benzaldehyde	52	48	48
2-Ethyl Hexanol	71	69	75
o-Nitrotoluene	56	56	49
Quinoline	68	58	68
Di-hexylether	83	83	70

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*See text for full explanation. Procedure a involves a total of 3 reductions to a final volume of 1 mL, while b involves a total of 4 reductions.

VII. ELUTION PATTERNS IN LEVEL 1 LC

A. Model Compounds

Several sets of mixtures of pure compounds were prepared to evaluate the elution patterns of the Level 1 LC separation (1). The mixtures were generally applied to the columns at levels corresponding to <25 mg of each compound to avoid overloading the column and therefore distorting the separation.

Table 14 shows the results of the first such experiment. The data illustrate a phenomenon that has been borne out in subsequent work: it is uncommon to find any given material isolated in one LC fraction. Several years of cumulative experience with the Level 1 LC separation have led to the inference that the band-broadening in this low resolution chromatographic method leads to elution peaks that are about one LC fraction wide.

Table 15 shows the results of LC elution pattern studies on a total of 17 model compounds. Based on these data and on observations of elution patterns in real samples subjected to Level 1 separation, Table 16 was prepared to indicate the most probably LC fractions for various compound categories. It should be emphasized that, because of band spreading and the low resolution separation, each of the indicated assignments should be regarded as uncertain to within 1 LC fraction.

Even the most polar compounds (e.g., p-toluene sulfonic acid) tested in the LC elution experiments were found in Fractions 6 and 7, and not in Fraction 8. Furthermore, the early pilot tests of the Level 1 methodology sponsored by Process Measurements Branch found no organic materials in Fraction 8. For these reasons, it was determined by PMB that LC 8 should be dropped and the LC separation be limited to 7 fractions.

TABLE 14

DISTRIBUTION OF MODEL COMPOUNDS AMONG LC FRACTIONS

Column spiked with 5 mL of solution containing four model compounds:

Cumene	4.7 mg/mL
Benzaldehyde	8.7 mg/mL
2-Ethyl-1-Hexanol	4.4 mg/mL
N-Methyl aniline	3.4 mg/mL

Fract. No.	Solvent	Distribution in Column Effluent			
		Cumene	Benzaldehyde	N-Methyl Aniline	2-Ethyl Hexanol
1	Pentane				
2	20% CH_2Cl_2 in Pentane	82%			
3	50% CH_2Cl_2 in Pentane	17%	22%		
4	CH_2Cl_2		75%		
5	5% CH_3OH in CH_2Cl_2		3%	3%	
6	20% CH_3OH in CH_2Cl_2			94%	99%
7	50% CH_3OH in CH_2Cl_2			2%	0.7%

TABLE 15

% DISTRIBUTION IN LC FRACTIONS

Compound	1	2	3	4	5	6	7	8	Ref.
Hexadecane	85	15							18
Cumene		82	17						18
Dichlorobiphenyl	25	69	5						18
Acenaphthene		69	31						18
Tetrachloroethane		81	19						18
o-Nitrotoluene			30	70					18
Dibenzofuran			∿100						13
Benzaldehyde			22	75	3				18
Dihexyl ether			18	77	4				18
N-methyl aniline					3	94	2		18
Quinoline						100			18
Diethyl Phthalate						100			18
2-Ethyl hexanol						99	0.7		18
Phenol						100			18
2-Hexanone						∿100			13
Acetophenone						∿100			13
p-Toluene sulfonic acid						27	68		13

TABLE 16

CATEGORIES FOR REPORTING OF LRMS DATA

Category (Subcategory)	Most Probable LC Fraction*
Aliphatic Hydrocarbons	1
(Alkanes)	1
(Alkenes)	1
(Alkynes)	1
Halogenated Aliphatics	1,2
(Saturated)	1,2
(Unsaturated)	1,2
Aromatic Hydrocarbons	2,3
(Benzenes)	2,3
Halogenated aromatic hydrocarbons	2,3
Nitro aromatic hydrocarbons	4,5
Fused alternate, non-alternate hydrocarbons	2,3
MW < 216 (methyl pyrene)	2,3
MW > 216	2,3
Ethers	4
(Halogenated Ethers)	4
Epoxides	4
Aldehydes and Ketones	4
Heterocyclic Oxygen Compounds	3,4
Nitriles	4
(Aliphatic)	4
(Aromatic)	4
Alcohols	6
(Primary, Secondary, Tertiary)	6
(Glycols)	6
Phenols	6
(Alkyl, etc.)	6
(Halogenated Phenols)	6
(Nitrophenols)	6
Esters	6
(Phthalates)	6
Amines	6
(Primary, Secondary, Tertiary)	6
(Hydrazines, azo compounds)	6
(Nitrosoamines)	6
Heterocyclic Nitrogen Compounds	
(Indoles, Carbazoles)	4
(Quinolines, Acridines)	6
Alkyl Sulfur Compounds	6
(Mercaptans)	6
(Sulfides, disulfides)	6
Heterocyclic Sulfur Compounds	
(Benzothiophenes)	4
Sulfonic Acids, Sulfoxides	7
Amides	6
Carboxylic Acids	6,7
Silicones	2,3,4
Phosphates	5,6,7

*Possible assignments. Fraction 4-5, 5-6, 6-7 generally overlap to a considerable extent.

B. Sodium Sulfate Drying of Extracts for LC

There was concern that the presence of water in Level 1 organic extracts was leading to irreproducible deactivation of the silica gel and, therefore, to irreproducible results of the LC separation. Experimental results indicated that sodium sulfate may be used as a drying agent for methylene chloride extracts without causing unacceptable losses of sample components.

A sample solution of model organic compounds was diluted to approximately 1000 ppm total concentration with methylene chloride. This was used as the stock solution. Sodium sulfate (Fisher certified ACS grade) was sequentially soxhlet extracted for 24 hours each with methanol, methylene chloride and pentane. After drying at 110°C for several days and cooling in a dessicator, the sodium sulfate was dry-packed into a column 2.5 cm in diameter (with fritted glass disk) to a depth of $\sim$3.0 cm. This required $\sim$12 gms of sodium sulfate. Aliquots of the stock solution were passed through the column. The eluent was collected and analyzed. Samples were analyzed by gas chromatography using the Level 1 TCO procedure.

Table 17 presents data for recovery of model compounds from dry methylene chloride extracts. Table 18 presents comparable data for recovery of model compounds from methylene chloride solutions that had been saturated by shaking with water. In each experiment, the total TCO value was unchanged, within 10%, by passing the sample through the sodium sulfate column.

The Level 1 LC column preparation procedure was, therefore, modified by adding a short bed of sodium sulfate at the top of the silica gel to dry the sample immediately prior to the separation.

TABLE 17

RECOVERY OF TCO AND OF SEVERAL MODEL COMPOUNDS* FROM SODIUM SULFATE COLUMNS: DRY SOLUTIONS

		% Recovery
Experiment 1		
Peak 1		109
Peak 2		106
Peak 3		98
Peak 4		101
	Total TCO	103
Experiment 2		
Peak 1		89
Peak 2		97
Peak 3		101
Peak 4		102
	Total TCO	97

---

*Model Compounds were identified only by retention times in these Experiments. Both polar and non-polar species were included.

TABLE 18

RECOVERY OF TCO AND OF SEVERAL MODEL COMPOUNDS FROM SODIUM SULFATE COLUMNS: WET SOLUTIONS

		% Recovery
Experiment 1		
Peak 1		122
Peak 2		130
Peak 3		101
Peak 4		99
Peak 5		99
Peak 6		106
Peak 7		106
Peak 8		119
Peak 9		106
	Total TCO	110
Experiment 2		
Peak 1		92
Peak 2		91
Peak 3		84
Peak 4		95
Peak 5		94
Peak 6		95
Peak 7		95
Peak 8		97
Peak 9		108
	Total TCO	96

C. LC Column Blank Due to Silica Gel

It was suspected that the most polar solvents used in the LC scheme might dissolve some of the silica gel from the column bed, giving rise to spurious high values in the gravimetric analysis. The following data were obtained for blank columns with no sample added:

Run No.	Fraction No. 7
1	1.0 mg
2	1.2
3	0.8
4	0.7
mean and standard deviation	0.9 ± 0.2 mg

No weighable material was found in any of fractions 1 through 6.

In an attempt to determine whether the silica gel could be separated from any sample components of fraction 7, the residues in the dishes were washed with hexane and the solvent was decanted. The washing was repeated with methylene chloride. The data below verify that only small quantities of silica gel are suspended in those solvents in this procedure.

	Fraction No. 7
original wt, mg	0.9 ± 0.2
after hexane, mg	0.8 ± 0.2
after CH_2Cl_2, mg	0.7 ± 0.2

It appeared to be necessary to correct the apparent weights of fraction 7 arithmetically, by subtracting the appropriate blank value, rather than by actually separating the sample from the silica gel.

VIII. RUGGEDNESS TESTING OF LEVEL 1 LC PROCEDURE

It was desirable to determine the change in results of the LC separation that might occur if a slight deviation in procedure was made. This margin of error within which an experiment can be varied and the results remain unchanged is commonly referred to as the ruggedness of the experiment. If the procedure could be done slightly differently each time and the same results obtained, chance are increased that intralaboratory or even interlaboratory results will be consistent and comparable.

The Level 1 LC procedure was studied for "ruggedness" in three different aspects.

- continuity of elution
- exact composition of eluants
- activity of silica gel

In all cases a solution of model compounds with a convenient elution pattern was employed to test the procedures. The fractions were analyzed by GC using the Level 1 TCO program and compared to controls.

To determine whether the continuity of elution affected the separation pattern of the LC, a column was run with a 0.5 hr break after fraction 4 and before fraction 5. The results show no significant change in the elution pattern in comparison to the LC procedure with no break outside the error associated with the LC procedure. (Figure 10.)

The stability of the LC separation relative to exact eluant composition is of interest for storing the solvents. It is convenient to be able to keep the solvent mixtures for several weeks and thus reduce preparation time for the LC procedure. This parameter was monitored both from the view of solvent composition change with time and LC separation change with time. The solvent mixtures were stored in amber bottles and tightly capped.

TEST LC: LC INTERRUPTED FOR 0.5 HOURS BETWEEN FRACTIONS 4 AND 5

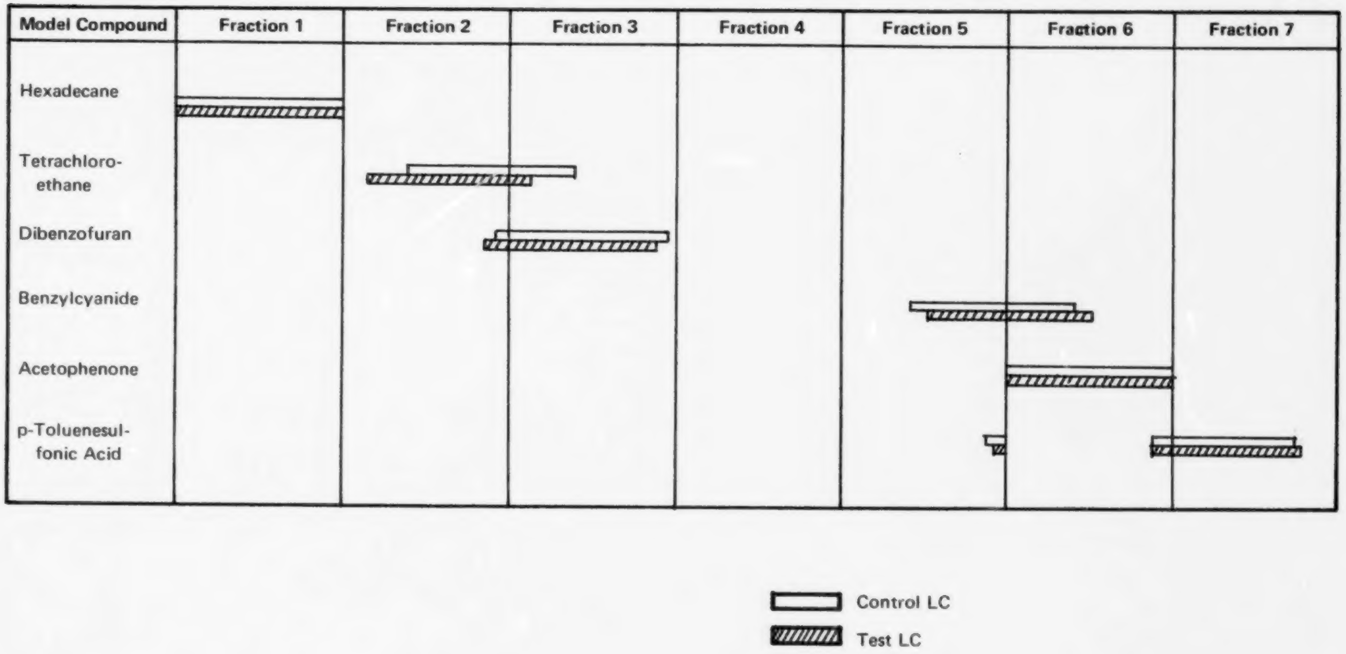


FIGURE 10 DISTRIBUTION OF MODEL COMPOUNDS IN THE LC SCHEME WITH MODERATE CHANGE IN PROCEDURE

The composition of the LC solvent mixtures changed very little over the testing period of four weeks. The largest variation observed was an increase in methanol percentage in fractions 6 and 7 of approximately 8%, as shown in Table 19.

The LC separation, as expected, also did not change significantly over the four week period. The results are shown in Figure 11.

The state of activity of the silica gel may affect the elution sequence. The effects of moderate variations in the duration and temperature of thermal activation and in the time the silica gel is stored after activation were tested.

- The silica gel was activated for 24 hours at 110°C, instead of the prescribed two hours, cooled in a dessicator and used immediately. The LC separation showed insigificant difference when compared to a separation done on silica gel activated for the usual two hours (Figure 12).

- The silica gel was activated for two hours at 100°C, but cooled for 16 hours in a dessicator, rather than just until cool enough to use. The pattern of LC elution was unchanged from the control LC with silica gel cooled for the minimum amount of time (Figure 13).

- Silica gel activated for two hours at 100°C was cooled in the ambient air rather than a dessicator and compared with silica gel cooled in a dessicator. The LC separation differed by an insignificant amount between control and air cooled silica gel (Figure 14).

- The activation temperature of the silica gel was tested at 90°C and 200°C. The separation at each temperature correlated very closely with the control activated at 100°C (Figures 15 and 16).

TABLE 19

CHANGE IN LC SOLVENT COMPOSITION WITH TIME

	FRACTION NO.						
SOLVENT	1	2	3	4	5	6	7
Fresh							
Methanol					5.8%	15.1%	45.9%
Methylene Chloride		19.8%	59.6%	100%	94.2%	84.9%	54.1%
Pentane	100%	80.2%	40.4%				
Two Weeks Old							
Methanol					7.1%	20.9%	44.9%
Methylene Chloride		19.3%	54.8%	100%	92.9%	79.1%	55.1%
Pentane	100%	80.7%	45.2%				
Four Weeks Old							
Methanol					6.8%	22.7%	52.3%
Methylene Chloride		20.9%	52.3%	100%	93.2%	77.2%	47.7%
Pentane	100%	79.1%	47.7%				

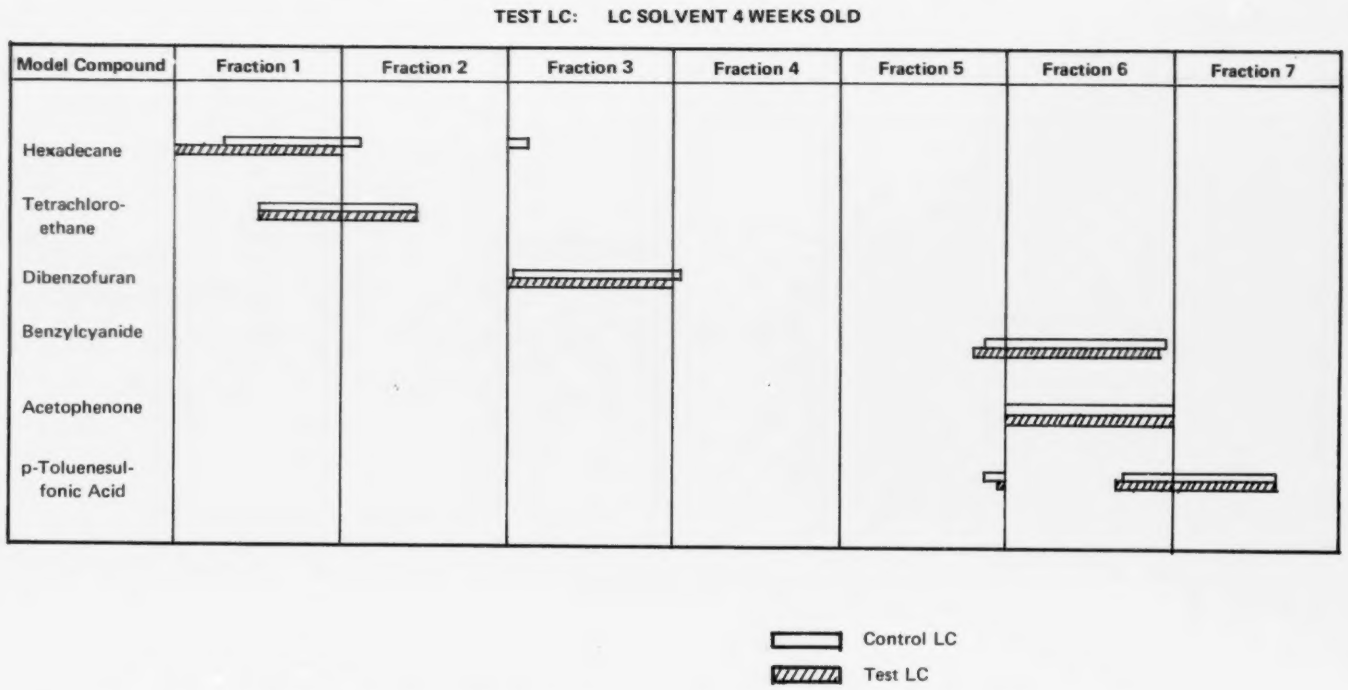


FIGURE 11 DISTRIBUTION OF MODEL COMPOUNDS IN THE LC SCHEME WITH MODERATE CHANGE IN PROCEDURE

TEST LC: SILICA GEL ACTIVATED FOR 24 HOURS

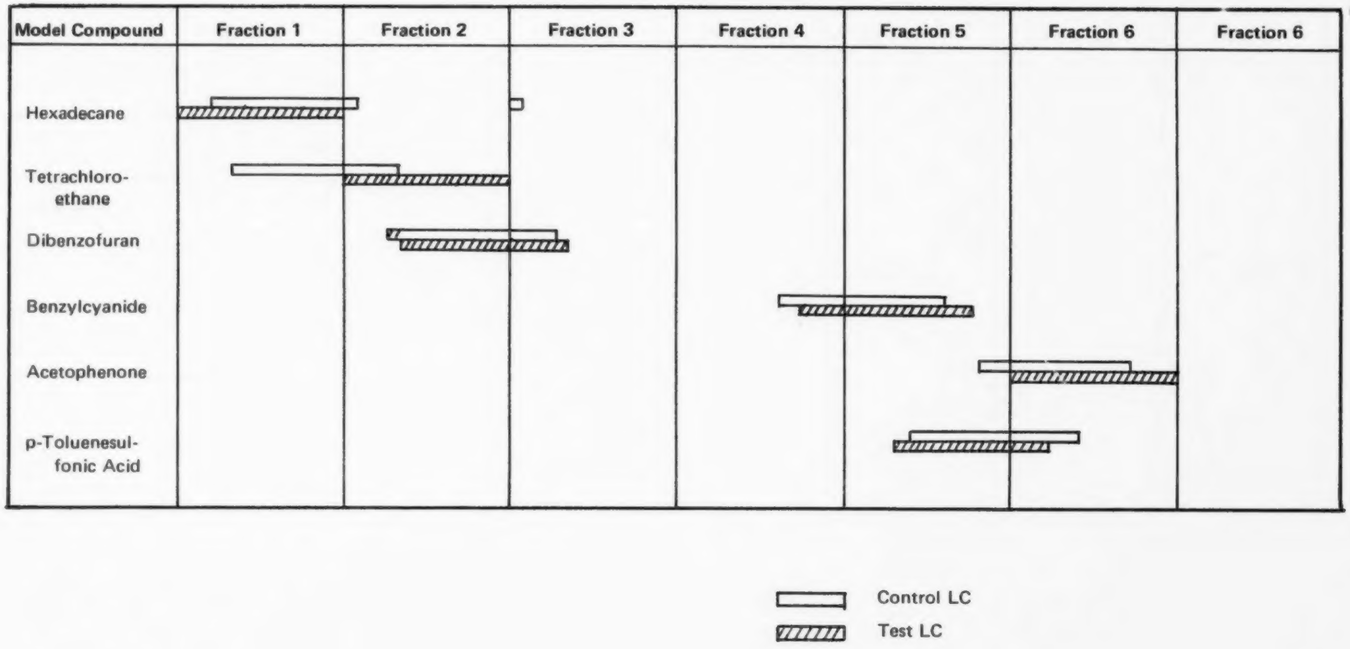


FIGURE 12 DISTRIBUTION OF MODEL COMPOUNDS IN THE LC SCHEME WITH MODERATE CHANGE IN PROCEDURE

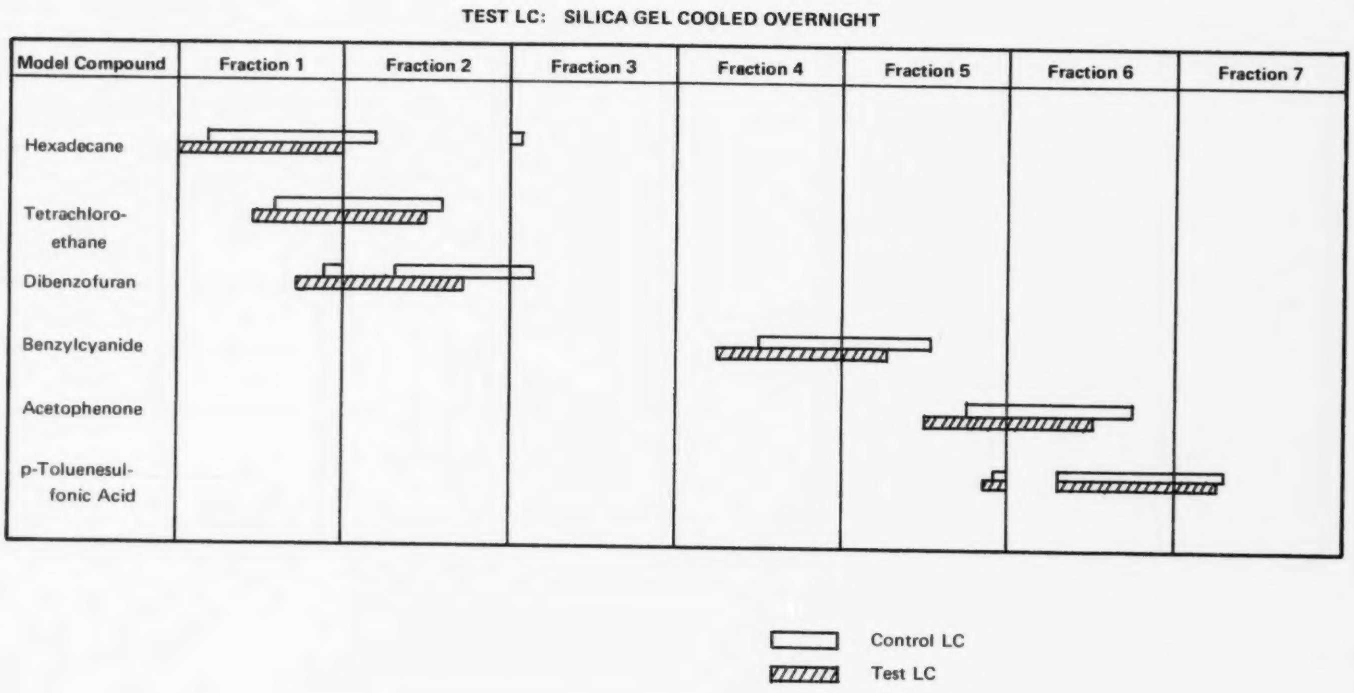


FIGURE 13 DISTRIBUTION OF MODEL COMPOUNDS IN THE LC SCHEME WITH MODERATE CHANGE IN THE PROCEDURE

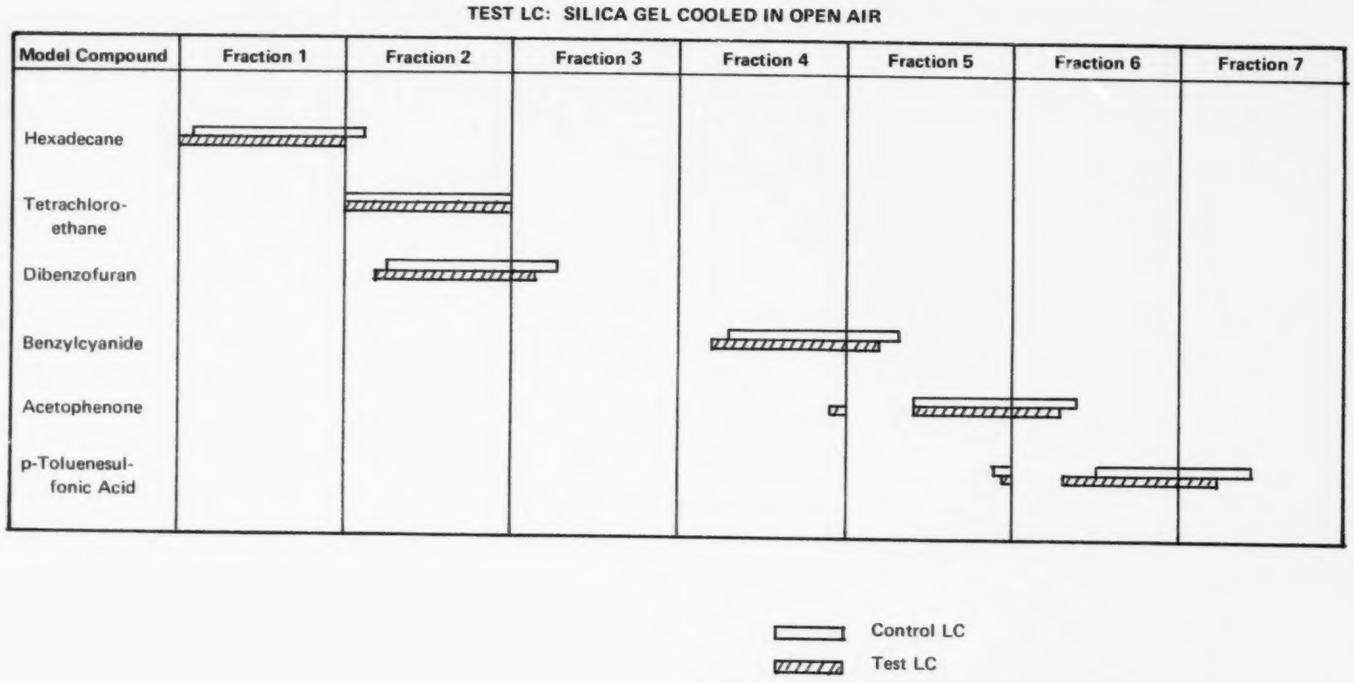


FIGURE 14 DISTRIBUTION OF MODEL COMPOUNDS IN THE LC SCHEME WITH MODERATE CHANGE IN PROCEDURE

TEST LC: LC SILICA GEL ACTIVATED FOR 2 HOURS AT 90°C

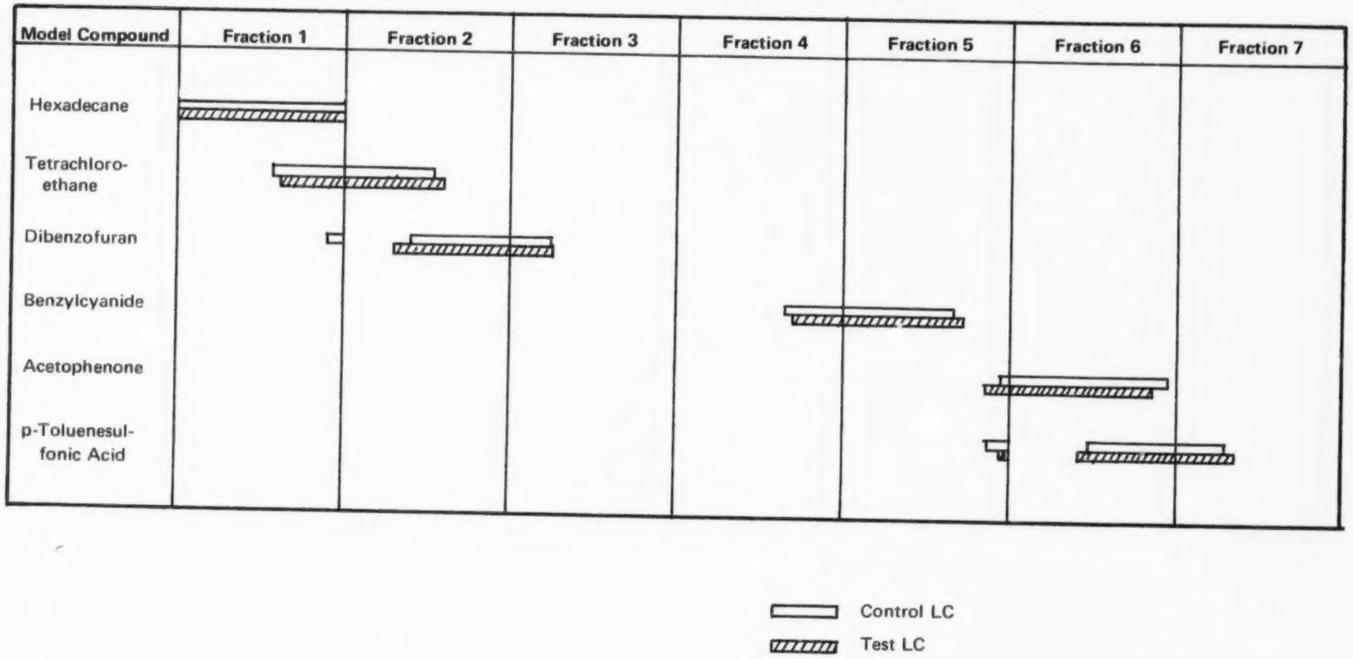


FIGURE 15 DISTRIBUTION OF MODEL COMPOUNDS IN THE LC SCHEME WITH MODERATE CHANGE IN PROCEDURE

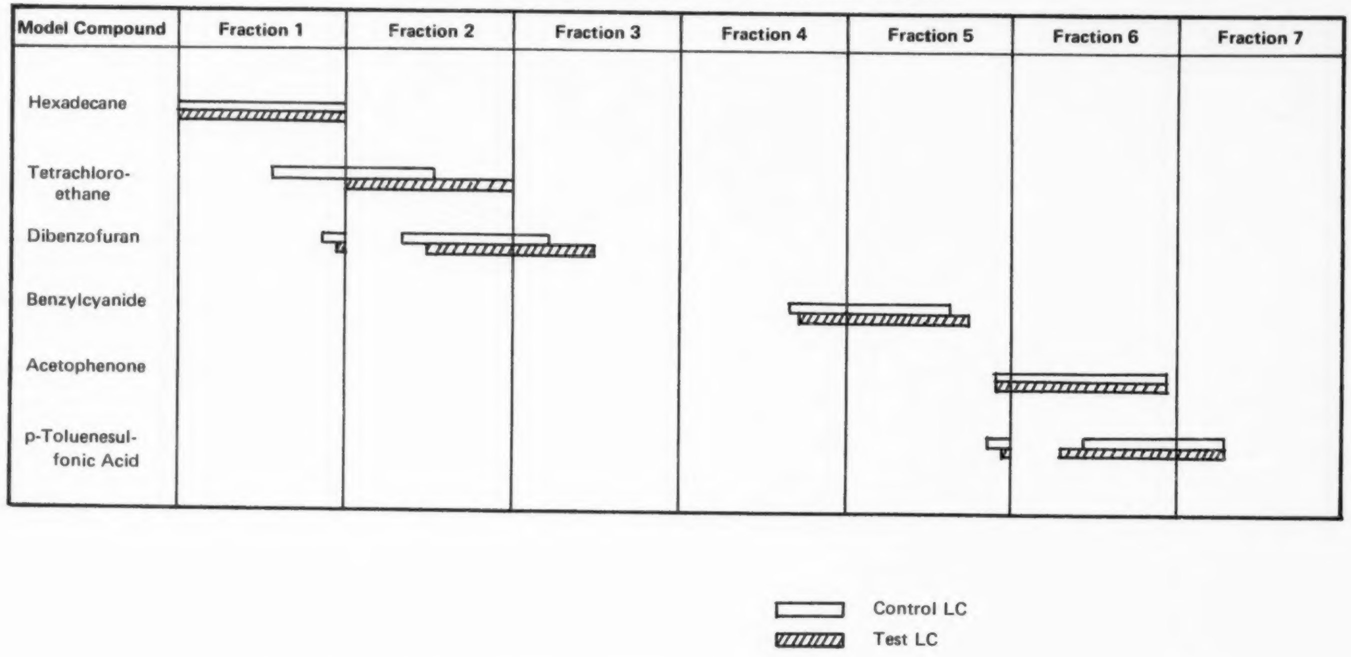

TEST LC: SILICA GEL ACTIVATED FOR 2 HOURS AT 200°C

FIGURE 16 DISTRIBUTION OF MODEL COMPOUNDS IN THE LC SCHEME WITH MODERATE CHANGE IN PROCEDURE

None of the experiments done to test different activation procedures of the silica gel showed a significant difference in LC separation from control samples run concurrently.

To evaluate the potential effects of variations in LC column temperature, five LC columns were run using the same solution of model compounds and with all conditions identical except for jacket temperature. Four jacketed columns were held at 14.5, 18, 20 and 22°C. The fifth column was run using acetone-cooling applied as described in the early versions of the LC method.

No significant changes were observed to result from these temperature variations. Figure 17 shows the elution pattern observed for the highest and lowest water jacket temperatures and for the acetone cooling. It is clear that over this temperature range, the elution behavior of each model compound was not altered by as much as one fraction.

Finally, a LC was done without solvent exchanging the sample from methyline chloride into cyclopentane to observe directly the effect incurred. The sample showed significant differences compared to the control. Most noticeable was a shift of the model compound eluting in fraction 2, to eluting in fraction 1 (Figure 18).

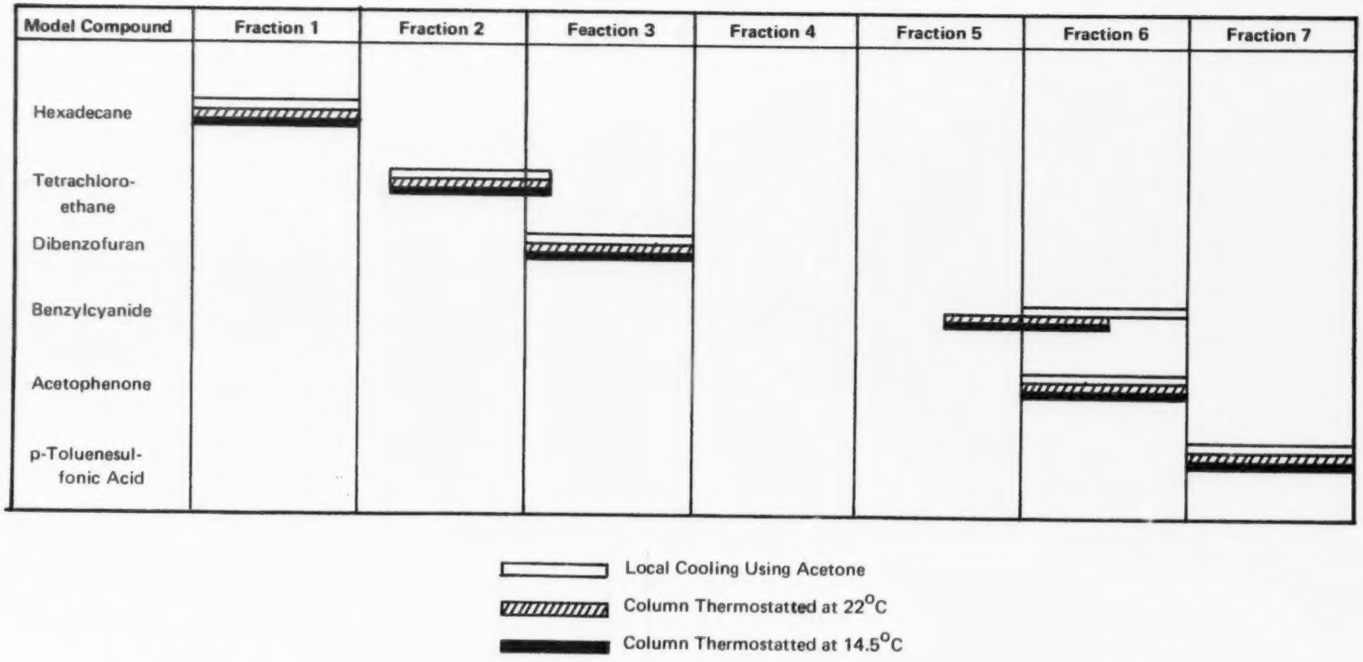
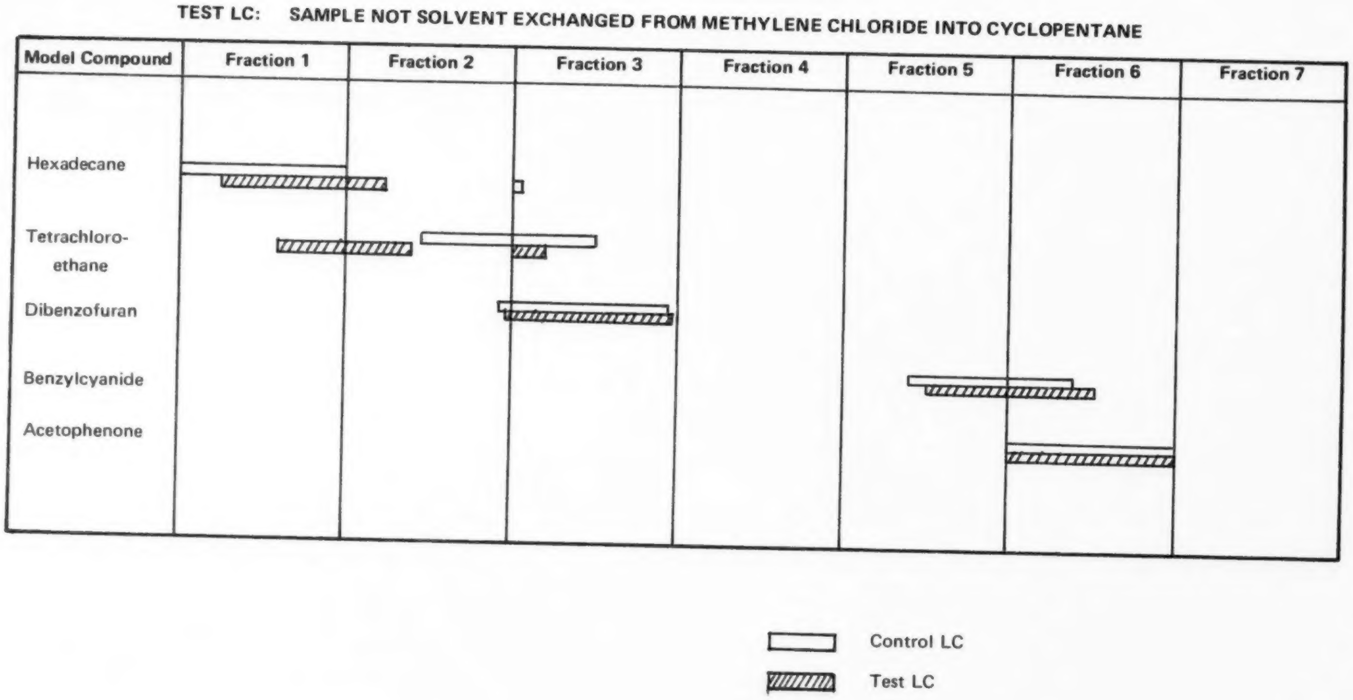

Model Compound
Fraction 1
Fraction 2
Feaction 3
Fraction 4
Fraction 5
Fraction 6
Fraction 7
Hexadecane
Tetrachloro-ethane
Dibenzofuran
Benzylcyanide
Acetophenone
p-Toluenesulfonic Acid
Local Cooling Using Acetone
Column Thermostatted at 22°C
Column Thermostatted at 14.5°C

FIGURE 17



TEST LC: SAMPLE NOT SOLVENT EXCHANGED FROM METHYLENE CHLORIDE INTO CYCLOPENTANE

FIGURE 18 DISTRIBUTION OF MODEL COMPOUNDS IN THE LC SCHEME WITH MODERATE CHANGE IN PROCEDURE

IX. REPORT FORMATS FOR LEVEL 1 ORGANIC ANALYSIS RESULTS

A. Introduction

A particularly important aspect of the evaluation and evolution of the Level 1 organic analysis procedures was the development of systematic reporting formats that summarize and integrate the data in a useful way. The report formats developed in this study have been incorporated into the Second Edition of the Level 1 Procedures Manual. (4) They are described briefly in this chapter and examples are given in Chapters X and XI.

Table 20 lists the major types of samples that are encountered in Level 1 organic analysis and indicates the data that are to be generated for each. In interpreting and integrating the Level 1 organic analysis data and reporting the results, a list of organic compound categories, based on the Multimedia Environmental Goals (MEG) (6) categorization scheme (slightly modified), is used to provide a means of organizing the Level 1 data. It should be emphasized that it is the list of MEG categories, and not the list of specific MEG compounds, that is referred to in the context of Level 1 organic analysis. With the addition of a very few non-MEG compound classes, this list of categories represents almost all of the organic chemistry likely to be encountered in most sources.

In developing this report format for Level 1 organic analysis results, the working assumption was that the users of Level 1 EA data will be interested in comparing estimated mass loadings in various streams with decision criteria expressed as concentrations. This is the type of approach, for example, that is incorporated in the SAM models (7) being developed for IERL, using DMEG (6) values as decision criteria. The format, however, is flexible enough for use in other models and with other decision criteria.

TABLE 20

SUMMARY OF EXPECTED DATA FROM LEVEL 1 ORGANIC ANALYSIS

SAMPLE	On-Site GC	TCO	GRAV	IR	LC*
Gases - Grab Sample	✓				
SASS					
>10 μm particulate			✓	✓	✓
3-10 μm particulate			✓	✓	✓
1-3 μm particulate			✓	✓	✓
<1 μm particulate			✓	✓	✓
Rinse of particulate modules			✓	✓	✓
XAD-2 Resin combined with rinse of sorbent module		✓	✓	✓	✓
Sorbent Module Condensate		✓	✓	✓	✓
SOLIDS					
Flyash; Clinker			✓	✓	✓
Organic Feed Stock		✓	✓	✓	✓
Coal		✓	✓	✓	✓
LIQUIDS					
Effluent Water		✓	✓	✓	✓
Organic Feed Stock		✓	✓	✓	✓
Fuels		✓	✓	✓	✓

*Includes GRAV + IR on all fractions; TCO and LRMS when sample quantity is sufficient.

A requirement of the approach is that all of the data reduction steps described in this document will be performed by personnel who have access to the original Level 1 organic analysis data and/or direct communication with the original analyst(s). The reason for this is that the organic analysis data outputs (i.e., spectra) contain a great deal of information (i.e., presence or absence of particular peaks) that is not easily reduced to tables or other forms intelligible to nonchemists, but is very valuable in making an assessment of the Level 1 sampling and analysis results. It is recognized, however, that guidance as to the appropriate models and decision criteria (concentrations) for comparison with the Level 1 data will usually be provided by others. For purposes of illustration (only), a SAM-1A type model has been used along with DMEG values as decision criteria in this report.

B. Results of the LC Fractionation

The results of the LC fractionation procedure include quantitative estimates of TCO* and GRAV range materials in each of seven fractions. In most cases, the quantity of material actually taken for the LC separation is only a portion of the total sample, and the amount taken should be stated in the report. The actual, measured TCO and GRAV values for the LC fractions should be multiplied by the appropriate factor (total sample quantity ÷ quantity taken for LC) to give the corresponding total sample values. It is then useful to convert these quantitative estimates into equivalent concentrations at the source, in order to facilitate comparisons with various decision criteria. Table 21 illustrates the format for reporting LC fractionation data. GRAV analyses involve weighing to the nearest 0.1 mg. TCO values and all Level 1 concentration data are reported to 1 or 2 significant figures.

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*On sorbent module extracts and other extracts or organic liquids found to contain more than 2 mg of TCO prior to LC fractionation. TCO analyses are not done on SASS particulate, ash, or clinker samples.

TABLE 21

LEVEL 1 LC RESULTS REPORT FORM

SAMPLE:

	TCO mg	GRAV mg	TCO + GRAV Total mg	Concentration mg/ (m^3, L, or kg)
Total Sample[1]				
Taken for LC[2]				
Recovered[3]				

Fraction	TCO in mg				GRAV in mg				TCO + GRAV Total mg	Concentration mg/ (m^3, L, kg)
	Found in Fraction	Blank	Cor-rected	Total[4]	Found in Fraction	Blank	Cor-rected	Total[4]		
1										
2										
3										
4										
5										
6										
7										
Sum										

1. Quantity in entire sample, determined before LC
2. Portion of whole sample used for LC, actual mg
3. Quantity recovered from LC column, actual mg
4. Total mg computed back to total sample

The Level 1 LC separation scheme is based on differences in polarity among various organic compound classes. Table 22 lists the compound classes that can be expected to be found in the LC fractions. The LC separation is not a high resolution technique and is not sufficiently precise to serve as a reliable qualitative identification tool. Considerable blurring between fractions is inevitable for complex samples. However, the LC separation scheme can and should be used to guide the interpretation of the LRMS and IR spectra. For example, an apparent "aliphatic hydrocarbon" moiety in LC6 could be an aliphatic acid, alcohol, amine, etc., but not a paraffin.

C. Results of the IR Spectroscopy

The total sample extract, or neat organic liquid, and the seven LC fractions are analyzed by IR spectroscopy. Spectra are interpreted in terms of the functional group types present in the major components of the sample or LC fraction. The many reference texts in this area are of considerable help in interpreting the IR spectra. The interpretation of the spectrum should also be guided by consideration of the LC fractionation scheme (Tables 3 and 22) and the LRMS results (when available). Components amounting to <5-10% of the total sample will not contribute significantly to the IR spectrum and cannot be detected by this technique.

The report format for the results of the IR analysis is shown in Table 23. Guidelines for reporting the data are:

1. Major peaks and assignments:

   - The frequency reported should be the peak maximum, or a range may be reported instead for broad peaks with no well-defined maximum.

TABLE 22

DISTRIBUTION OF ORGANIC COMPOUND CLASSES AMONG LC FRACTIONS

LC Fraction	Organic Classes Predominating	MEG List Category
1	Aliphatic Hydrocarbons	1
	Halogenated Aliphatics	2
2,3,4	Aromatic Hydrocarbons	15,21,22
	Halogenated Aromatics	16
4,5	Heterocyclic N,O,S Compounds	23,24,25
	Sulfides, Disulfides *	13B
	Nitriles *	9
	Ethers	3,4
5,6	Aldehydes, Ketones *	7
	Nitroaromatics	17
	Alcohols	5,6
	Amines	10,11,12
6,7	Alcohols	5,6
	Phenols, Halo and Nitrophenols	18,19,20
	Esters, Amides *	8C,8D
	Amines	10,11,12
	Mercaptans *	13A
	Carboxylic Acids	8A,8B
	Sulfoxides	14B

---

* These compound classes have not yet been tested in the LC scheme, so these assignments should be regarded as more tentative than the others.

TABLE 23

LEVEL 1 IR RESULTS REPORT FORM

IR REPORT

SAMPLE:____

Wave Number (cm^{-1})	Intensity	Assignment	Comments

- The intensity is reported relative to the strongest peak in the spectrum on a transmittance basis.
  s = strong - 50-100% of strongest peak
  m = medium - 20-50% of strongest peak
  w = weak - 5-20% of strongest peak
  When a peak is of borderline intensity, it should be labeled "m." Finer intensity ratings such as m-s or w-m are not appropriate.

- The assignment/comments column indicates the functional group(s) to which the peak is attributed. It may also contain single word descriptors of peak shape such as: "broad," "doublet," "shoulder."

2. Unassigned weak bands:

This data category is merely a list of frequencies, in cm^{-1}, of weak bands the analyst considers possibly significant but cannot assign to a particular functional group. Any medium or strong peak, even if unassigned, should be reported in Section 1 of the IR report.

3. Other remarks

This reporting point will not always be required. An example of the type of other remarks to be included is: "The IR does not confirm LRMS indication of quinones: no 1690-1660 cm^{-1} bands."

It is not necessary to report every peak in the IR spectrum. It is expected that ≤ 10 "major peaks and assignments" entries, and ≤ 6 "unassigned weak bands," will be typical.

D. Results of Low Resolution Mass Spectroscopy

Low resolution mass spectra (LRMS) are obtained on each LC fraction which has sufficient quantity, when referenced back to the source. All samples that meet the decision criteria for quantity (TCO plus GRAV) will require analysis via the direct insertion probe. Samples with significant quantities of TCO range material should also be analyzed by insertion in the batch inlet. The mass spectroscopist is encouraged to integrate the interpretation of the mass spectra obtained on a particular sample to provide one report describing sample chemistry.

Interpretation of the spectra is guided by knowledge of the LC separation scheme, the IR spectra, and other information about the source. In reporting the results of the LRMS analysis, the basic philosophy is to present increasingly more specific data, as the complexity (or simplicity) of the spectra will allow. The first level of reporting is to identify compound classes. If possible, or appropriate, one should then attempt to identify the subcategory compound classes present in the fraction. Finally, specific compounds should be identified if possible to do so from the spectra. Where possible, the molecular weight range and composition of each of the categories should be reported. The relative abundance of each category should be estimated with a rating of 100 = major, 10 = minor, 1 = trace.

It should be possibe, using this methodology, to account for nearly all observed species by selection from a relatively small list of compound categories and subcategories. A list of such categories has been assembled in Table 24. The primary reference for selecting these categories was the MEG list (6), which seems to do a good job of representing all probable major compound classes. Some few categories were not in the MEG list and have been added here.

TABLE 24

CATEGORIES FOR REPORTING OF LRMS DATA

Category (Subcategory)	MEG List Category No.	Probable LC Fraction*
Aliphatic Hydrocarbons	1	1
(Alkanes)		1
(Alkenes)		1
(Alkynes)		1
Halogenated Aliphatics	2	1,2
(Saturated)		1,2
(Unsaturated)		1,2
Aromatic Hydrocarbons		2,3
Benzenes	15	2,3
Halogenated aromatic hydrocarbons	16	2,3
Nitro aromatic hydrocarbons	17	4,5
Fused alternate, non-alternate hydrocarbons		2,3
MW < 216 (methyl pyrene)	21,22	2,3
MW > 216	21,22	2,3
Ethers		4
(Halogenated Ethers)	3,4	4
Epoxides	6	4
Aldehydes and Ketones	7	4
Heterocyclic Oxygen Compounds	25	4
Nitriles	9	4,?
(Aliphatic)		4,?
(Aromatic)		4,?
Alcohols	5,6	6
(Primary, Secondary, Teriary)	(5)	6
(Glycols)	(6)	6
Phenols	18	6
(Alkyl, etc.)		6
(Halogenated Phenols)	19	6
(Nitrophenols)	20	6
Esters	8C	6
Phthalates		6
Amines	10,11,12	6
(Primary, Secondary, Tertiary)	(10)	6
(Hydrazines, azo compounds)	(11)	6
(Nitrosoamines)	(12)	6

continued....

TABLE 24 (Continued)

Category (Subcategory)	MEG List Category No.	LC Fraction*
Heterocyclic Nitrogen Compounds	23	
(Indoles, Carbazoles)		4
(Quinolines, Acridines)		6
Alkyl Sulfur Compounds	13	6
(Mercaptans)		6
(Sulfides, disulfides)		6
Heterocyclic Sulfur Compounds		
(Benzothiophenes)	24	4
Sulfonic Acids, Sulfoxides	14	?
Amides	8C	6
Carboxylic Acids	8	6,7
Silicones		?
Phosphates		?
Pesticides		?
Dyestuffs		?

*Possible assignments. Fraction 4-5, 5-6, 6-7, generally overlap to a considerable extent.

The list in Table 24 is also organized somewhat differently than the MEG list to be more compatible with the nature of the mass spectrometry data. It should be strongly emphasized that the list probably does not include all compound categories that it will be possible for one to identify. If interpretation of the spectra yields the identification of a category not included in this table, the category should be reported. At the same time, EPA should be notified of the need to add that category to the list. It will be possible in most cases to identify the spectra in terms of the compound categories listed in Table 24, but one should avoid "force fits" to the categories if another one seems more appropriate.

Interpretation of the mass spectra data should take full advantage of all other information known about the same source, LC fraction and IR spectra. Since the LC separation does a reasonable job of dividing compound classes, the categories listed in Table 24 have been listed in order of their possible elution from the LC column. Where possible some indication has been made as to the LC fraction in which the category might elute. These fraction assignments are known to be correct in some cases and are only estimates in others. Sometimes the sample characteristics will have minor effects on the fraction elution behavior. Again the LC fraction indications should only be taken as a guideline.

Table 25 shows the report form for the LRMS data.

It is once again emphasized that interpretation of the LRMS data is best done using all available information such as what one knows about the chemistry of the source being sampled, what species generally elute in the LC fraction being examined and functional group data derived from the IR spectra.

TABLE 25
LEVEL 1 LRMS RESULTS REPORT FORM

LRMS REPORT

SAMPLE: ____________________

Major Categories

Intensity	Category	MW Range

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition

Other

E. Organic Analysis Summary Tables

At the end of the Level 1 organic analysis procedure, there will be an LC report, 8 IR reports, and up to 7 LRMS reports for each organic extract or neat organic sample. This is an unwieldy body of data from which to make a decision. The first step in reducing these data to a workable form is to prepare a single table that summarizes the organic analysis results for each extract. Table 26 illustrates this table and the following paragraphs describe the various entries.

Space is allotted in the table heading for a sample identification code. It was assumed that each laboratory will have devised its own coding system for uniquely identifying the various samples. It may be desirable to include the date, the name of the analyst, or other similar information as well.

The body of the table includes one column for each of the LC fractions and one column for summing of the data. The first set of data entries is the quantitative analysis results, transcribed from the LC report (Table 21). The calculated total organic loading, in mg/m^3, corresponding to each fraction is entered in the first row. This value is used in estimating the abundances of the various organic compound classes. The next two rows contain the estimated TCO and GRAV values, to indicate the distribution of total organics between volatile (b.p. 100-300°C) and nonvolatile (b.p. >300°C) materials. This information can be useful later in the selection of appropriate DMEG or other decision criteria values for comparison with the Level 1 results.

The results of the LRMS analyses are summarized in the table as follows. The major categories present (item 1 of Table 26) in LC1 are listed at the left-hand side of the table and the approximate intensity (100, 10, or 1) for each category is entered in the LC1 column. To convert the LRMS intensity index to a concentration estimate for each organic compound category, the individual intensity value is divided by the sum of all intensities for that LC fraction and then multiplied by the total organic

TABLE 26

LEVEL 1 ORGANIC EXTRACT SUMMARY TABLE

ORGANIC EXTRACT SUMMARY TABLE

Sample ______________________________

	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total Organics, mg								
TCO, mg								
GRAV, mg								

Category Assigned Intensity MG/

loading (mg/m^3) estimated for the fraction. This procedure is then repeated for the other LC fractions. Examples are worked in Figure 19 for two LC fractions, LC2 and LC4, of the same XAD-2 extract.

The results presented in Figure 19 illustrate the considerable overlap in chemical class composition that can be expected between some fractions in the Level 1 LC scheme. As noted earlier, this is not a high resolution separation technique and the various compound categories cannot be uniquely assigned to particular LC fractions. The data do show the expected trend, in that LC2 is relatively richer in light aromatics (benzene and fused species with MW <216) than is LC4. The fact that adjacent LC fractions can be expected to show gradual changes in chemistry can serve as a useful guide for the analyst in detecting contamination. Very abrupt changes in apparent composition, or the appearance of a compound class in an entirely unexpected fraction (i.e., phthalates in LC2 or paraffins in LC6) should be regarded with suspicion.

The overlap between fractions can also be used in estimating the composition of those fractions which did not contain sufficient material to trigger an LRMS analysis. For any LC fraction that was not analyzed by LRMS, it is suggested that the IR spectrum be compared with the IR's of the adjacent fractions. If a close correlation is found between two IR spectra then this, together with the known behavior of the LC scheme, suggests that the two LC fractions have similar, though not identical, qualitative composition. It is therefore proposed that the total organics in the non-LRMS LC fraction be distributed over the same classes and in the same proportion as was done for the adjacent LC fraction whose IR spectrum was the best match. The error introduced by this procedure into the overall description of sample chemistry will be small, since only fractions with small amounts of material are excluded from the LRMS.

Concentrations estimated by this procedure should be identified with an asterisk in the organic extract summary table and an explanatory footnote included.

LC 2

Total organics = 0.57 mg/m^3

Aromatic HC's-benzenes	10
Fused Arom <216 MW	100
Fused Arom >216 MW	10
Heteroyclic S Compounds	10

LC 4

Total organics = 6.6 mg/m^3

Fused Arom <216 MW	100
Fused Arom >216 MW	100
Heterocyclic S Compounds	10
Heterocyclic O Compounds	10

Calculation of Concentration Estimates by Category

$\sum$ intensities = 130

Aromatic HC's - benzene: $\frac{10}{130} \times 0.57 = 0.04\ mg/m^3$

Fused Arom <216 MW: $\frac{100}{130} \times 0.57 = 0.4\ mg/m^3$

Fused Arom >216 MW: $\frac{10}{130} \times 0.57 = 0.04\ mg/m^3$

Heterocyclic S Cmpds: $\frac{10}{130} \times 0.57 = 0.04\ mg/m^3$

$\sum$ intensities = 220

Fused Arom <216 MW: $\frac{100}{220} \times 6.6 = 3\ mg/m^3$

Fused Arom >216 MW: $\frac{100}{220} \times 6.6 = 3\ mg/m^3$

Heterocyclic S Cmpds: $\frac{10}{220} \times 6.6 = 0.3\ mg/m^3$

Heterocyclic O Cmpds: $\frac{10}{220} \times 6.6 = 0.3\ mg/m^3$

FIGURE 19. EXAMPLE CALCULATIONS OF CONCENTRATION ESTIMATES FROM LRMS DATA

If it is not possible to relate the composition of an LC fraction to LRMS data, either directly or by analogy to another LC fraction, then it will not be possible to describe the LC fraction chemistry with the same degree of specificity. If only the IR and LC analyses are performed, a compromise procedure might be to: 1) List all categories that could be in that fraction chosen from Tables 3 and 4; 2) Assign an intensity of 100 to each category for which functional groups were identified in the IR; and 3) Assign an intensity of 10 to each category for which functional group frequencies were not identified. Then, in the absence of evidence to the contrary, assume that categories with an intensity of 100 may constitute up to 50% of the total sample and those with an intensity of 10 up to 10%. Clearly, this procedure will "account for" more than 100% of the total sample. However, this conservative method of estimation seems necessary because it is not possible to determine from the IR spectrum of a mixture how the various functional groups are assembled into molecules or classes.

Figure 20 illustrates this procedure for an LC6 sample, assuming only IR and LC data were available. Concentrations estimated on the basis of IR and LC data only should be marked with a double asterisk in the organic extract summary table and an explanatory footnote should be included.

Once concentrations have been estimated for all compound categories identified in the seven LC fractions for a particular organic extract, or neat organic liquid, these values are summed across each row of the table. This procedure condenses the information obtained on the various LC fractions to provide an integrated description of the chemical composition of the organic extract. It is inappropriate to state the concentrations of various categories to more than one significant figure at this stage of the data reduction. Examples of completed organic extract summary tables are given in Chapters X and XI.

Sample LC 5 Total Organics = 0.28 mg/m^3

IR Report $\bar{\nu}$, cm^{-1}	I	Assignment/Comments	Categories Possible in LC 5	Assigned Intensity	Maximum Possible Concentration
3400	S	OH or NH/Broad	Heterocyclic N compounds	100	0.14 mg/m^3
3050	M	Aromatic CH	Heterocyclic O compounds	100	0.14
2850-2950	S	Aliphatic CH	Heterocyclic S compounds	10	0.01
2230	M	C N or C≡C	Sulfides, Disulfides	10	0.01
1700	S	Ketone, Carboxylic acid	Nitriles	100	0.14
1600	S	Conj. C C or aromatic C N, N-NO$_2$, C-N=O Carboxylate	Ethers	100	0.14
1530	M	C-N, C-NO$_2$	Aldehydes, ketones	100	0.14
1420-1450	S	CH$_3$, NH$_4^+$	Nitroaromatics	100	0.14
1050-1300	M	Multiple peaks	Alcohols	100	0.14
700-850	S	Subst. benzene rings	Amines	100	0.14

FIGURE 20. ESTIMATION OF FRACTION COMPOSITION FROM IR AND LC DATA ONLY

If the organic analysis results summarized in the last column of Table 26 were for a neat organic liquid sample or for the extract of an aqueous or solid process or effluent stream, then the "Σ" data would be appropriate for comparison with MATE values or other decision criteria as described in the next section. If, however, the results in Table 26 were for one of the several organic extracts obtained for a single SASS train sample, the "Σ" data for each of the extracts should be pooled to yield one estimate of stream chemistry for comparison with decision criteria. Table 27 indicates a format for that summary table. If the criteria concentrations are exceeded, of course, it is possible to refer to the data in Table 27 to determine whether the material of concern is in the particulate, vapor, or both.

F. Comparison with Decision Criteria

The previous section has described a set of procedures for interpreting and integrating the Level 1 organic analysis data. The results of those procedures is a list of organic compound classes and estimated streams sampled. These concentrations can be compared with appropriate decision criteria values in making a Level 1 environmental assessment decision. If one or more of the estimated concentrations exceeds the levels of concern, it may then be desirable to reexamine the organic analysis in detail to determine more specifically the nature of the material responsible for the positive "trigger."

As noted in the introduction to this document, it can be assumed that many, if not most, users of EA data will be interested in using decision criteria such as DMEG values for effluent streams. The DMEG values are specific for individual chemical species, while the organic analysis results give concentration data for chemical categories. Prudence dictates that, for each chemical category, the DMEG value most appropriate for comparison is the value for the most hazardous compound (lowest DMEG value) in that category that could possibly be present in the sample. In many cases, especially when LRMS data were obtained, it will be

TABLE 27

SUMMARY OF RESULTS FOR ORGANIC EXTRACTS FOR SASS TRAIN SAMPLES

	Σ,* mg/m^3					
	Particulate Module			Sorbent Module		Total
	Rinses	>3 µm	<3 µm	Resin + Rinse	Condensate	
Total Organics						
CATEGORIES						
Sulfur						
Aliphatic HC's						
Aromatics - Benzenes						
Fused Aromatics <216						
Fused Aromatics >216						
Heterocyclic S						
Heterocyclic N						
Heterocyclic O						
Carboxylic Acids						
Phenols						
Esters						

*Sum of results for all LC fractions for each extract.

possible to rule out the presence of the "worst case" compound in a particular MEG category. The LRMS data may indicate, for instance, that the fused polynuclear aromatic hydrocarbons in a sample are all of MW <216 and that, therefore, one need not use the very low DMEG value for benzo[a]pyrene, MW 252, in category 21.

The recommended procedure would be as follows:

1. List the categories of compounds found in the stream, with MEG category number (Table 4) and estimated concentration.
2. For each MEG category listed above, identify the compound with the lowest DMEG value.
3. If the estimated concentration in the stream is lower than this DMEG value for a category, go on to the next category.
4. Review the data to see if there is any evidence that that compound cannot be present in the sample. This evidence may be LRMS data on MW ranges or compound types, such as the fact that amines present are not nitrosamines. Other evidence may be that the compound has a boiling point <100°C and therefore was not possibly present in an SASS sample.
5. If the compound with the lowest DMEG can be ruled out, identify the compound with the next lowest DMEG in that category and reiterate steps 3, 4, and 5 until DMEGs have been chosen for all categories identified in the sample.
6. The highest DMEG value in a MEG category becomes the default value, to use if all lower DMEG correspond to compounds not possibly present in the sample.
7. List compounds and DMEG values chosen as appropriate for each category.
8. Tabulate ratio of estimated concentration to DMEG value for all categories identified.

X. EXAMPLE OF APPLICATION OF LEVEL 1 PROCEDURES TO FUEL SAMPLES

A. Introduction

In designing the present phased approach to environmental assessment, the authors recognized the diagnostic importance of examining feedstocks and fuels -- the input material to industrial manufacturing and energy-producing processes -- in order to identify potential environmental pollutants at their source. Presumably, direct information of this kind would be useful in selecting and applying pollution control technology to those industrial processes, or in specifying and controlling the composition of fuels and feedstocks so as to minimize the amount of effluent control required in certain cases.

A 1977 report by L.N. Davidson *et al.*, "Technical Manual for the Analysis of Fuels," (8) identified the principal established methods for sampling and analysis of hydrocarbon fuels. Those methods were generally developed for the use of engineers concerned primarily with the efficient utilization of fuels as energy sources. While many of them are capable of providing valuable information about the composition of fuels, and particularly about components such as total sulfur, nitrogen and chlorine, and residual ash, they leave much to be desired from the standpoint of direct analysis for trace elements and for specific organic substances other than those constituting the fuel itself.

One approach to the identification and measurement of potential pollutants in fuels is to subject those fuels to an appropriately modified Level 1 and/or Level 2 analytical scheme. As an example of the kind of information that would be obtained from conducting the organic analysis portions of the Level 1 protocol on fuels, two sets of results are included here, pertaining to coal and to #4 fuel oil. Certain obvious limitations can be seen in the use of the Level 1 protocol on such samples, especially in regard to analysis for organic species. These limitations will be discussed, and some suggestions will be offered which should help, at least partially, to overcome them. These suggestions constitute the best guidance that can be offered at present for sampling and analysis of fuels beyond the use of conventional methods and of the Level 1 protocol.

B. Level 1 Sampling and Analysis of Fuels

The information obtainable from a complete Level 1 assay of fuel samples is likely to be useful in detecting potential pollutants in fuels or in identifying the source of such pollutants when they are discovered in effluent. To make best use of that information, however, one needs to know something about the chemical and/or physical processes to which the fuel will be subjected in the course of producing various kinds of effluents. For example, a pile of loose coal, standing uncovered and exposed to the weather, might produce a windblown dust which would be chemically unchanged and which might need to be considered only as an unreactive particulate. Leaching of the coal pile by rain could produce an aqueous leachate that might be contaminated with soluble ions such as sulfate and which might also be highly acidic and contain various dissolved trace elements in ionic form. Conversion of the coal to coke or to a liquid or gaseous form involves chemical as well as physical changes, and results in the production and/or liberation of some chemical species that would not be found by a Level 1 analysis of the original material.

Combustion of a solid or liquid fuel may produce a great variety of organic substances as well as a smaller variety or inorganic species, depending not only on the initial composition of the fuel but also on the conditions of combustion and of interaction between the effluents and the environment into which they are discharged. The large influence of these latter parameters (i.e., combustion and discharge) on the identities and quantities of emitted organic substances places severe limits on the value of any analysis of the composition of such a fuel for purposes of predicting the nature of its potential for environmental pollution.

The protocol for a Level 1 analysis calls for treatment of gaseous fuels as gases, to be collected as "grab" samples and analyzed accordingly by on-site GC. If, in addition, it were decided to determine whether a gaseous fuel might contain trace-level components in the higher-molecular weight range, the Level 1 gas analysis might be supplemented by a vapor analysis. A 30 m^3 sample might be passed through the sorbent (XAD-2) trap of a SASS train, just as if it were the mixture of air and combustion products in a stack effluent. Any material collected on the sorbent would then be removed and analyzed by the recommended procedure, involving liquid chromatography followed by infrared spectrophotometry, gas chromotography (TCO), gravimetry and low resolution mass spectrometry (LRMS).

Liquid fuels include, in addition to liquid petroleum fuels, shale oil, coal liquids and methyl fuels. The principal distinguishing characteristic of the last-named group is its miscibility with water, since methyl fuels consist essentially of methanol, and always contain small quantities of dissolved residual water. A Level 1 organic analytical procedure for any fuel should be carried out directly on a small sample of the fuel which can be treated as if it were a methylene chloride extract of a sorbent module or of a solid sample. If the fuel is a liquid petroleum product, the sample will consist primarily of aliphatic hydrocarbons. The Level 1 liquid chromatography (LC) procedure will, therefore, show predominantly high yields in fraction #1, with smaller but still substantial quantities appearing in fractions #2 and #3. Shale oils and coal liquids can also be expected to show large yields in these three fractions.

Methanol fuels will consist primarily of compounds that appear in fraction #6. Infrared and LRMS analysis of the fractions will help to characterize both the matrix materials and the minor components of all of these liquid fuels.

Analysis of coal fuels and other solid fuels by the Level 1 protocol may be limited value, as the foregoing discussion has suggested. The bulk of such fuels, although organic, is not readily soluble in ordinary liquid organic solvents under near-ambient conditions of temperature and pressure, even when the original sample is ground to a fine powder before extraction. The results of a Level 1 analysis of such fuels are, therefore, applicable only to the description of a minor portion of the total combustible fuel.

C. Level 1 Organic Analysis Results for a Fuel Oil Sample

An example of an actual Level 1 analysis of a liquid petroleum, #4 fuel oil, is summarized in Table 28. A 100 mg portion of the oil was applied directly to the Level 1 LC column, with no sample preparation. A separate portion was dissolved in pentane and analyzed according to the Level 1 TCO procedures. More than 98% of the fuel oil was found to be GRAV range material. The data show that the major organic components of #4 fuel oil are aliphatic hydrocarbons (68%), aromatic hydrocarbons (14%) and fused aromatic hydrocarbons in the molecular weight range below m/e = 216 (11%). Trace quantities of fused aromatic hydrocarbons of m/e > 216 were found, as well as traces of carboxylic acids.

The Level 1 LC, IR and LRMS reports which were integrated to produce the organic extract summary table are presented as Tables 29-39.

No TCO analyses were performed on the LC fractions for this sample because the TCO value for the unfractionated sample was less than 2% of the GRAV level. Therefore, the TCO portion of the LC report, Table 29, is left blank.

Comparison of the IR reports (Tables 30-33) with the LRMS reports (Tables 34-39), for the same fractions reveals no inconsistencies between the two types of qualitative analysis data. There is no LRMS report for LC 5 because the total quantity of material in this fraction (0.4 mg) was so small. The chlorinated hydrocarbon material identified in LC 6 by LRMS, confirmed by IR in LC 5, LC 6 and LC 7, was not reported in the organic summary table because it is thought to be a contaminant introduced in the laboratory. As indicated in Tables 16 and 24, chlorinated hydrocarbons are expected to elute in fractions LC 1, LC 2 and/or LC 3 of the Level 1

TABLE 28

ORGANIC EXTRACT SUMMARY TABLE FOR #4 FUEL OIL

Sample #4 Fuel Oil, 100 mg Analyzed

	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total Organics, mg/m^3								
TCO, mg *								
GRAV, mg	65	6.4	24	1.4	**0.4	1.9	0.3	100

Category Int/mg/m^3								
Aliphatic Hydrocarbons	100/65	10/3.2						68
Aromatic Hydrocarbons		10/3.2	100/11					14
Fused Aromatic Hydrocarbons m/e < 216			100/11					11
Fused Aromatic Hydrocarbons m/e > 216			10/2					2
Heterocyclic Nitrogen Compounds				100/1.3				1.3
Esters				10/0.1		1/0.6	1/0.1	0.8
Carboxylic Acids					**1/0.4	1/0.6	1/0.1	1.1

* Not done, due to the low content of volatile constituents.

**Concentration estimated from IR data only.

TABLE 29

LC REPORT FOR FUEL OIL

SAMPLE: No. 4 Fuel Oil (Undiluted)

	TCO mg	GRAV mg	TCO + GRAV Total mg	Concentration mg/ (m^3, L, or kg)
Total Sample[1]	< 2	100	100	N/A*
Taken for LC[2]		100	100	
Recovered[3]		100	100	

Fraction	TCO in mg				GRAV in mg				TCO + GRAV Total mg	Concentration mg/ (m^3, L, kg)
	Found in Fraction	Blank	Cor-rected	Total[4]	Found in Fraction	Blank	Cor-rected	Total[4]		
1	N/A				65.4	–		65	65	N/A
2					6.4	–		6.4	6.4	
3					24.2	–		24	24	
4					1.4	–		1.4	1.4	
5					0.4	–		0.4	0.4	
6					1.9	–		1.9	1.9	
7					1.2	0.9		0.3	0.3	
Sum					101.2			100	100	

1. Quantity in entire sample, determined before LC
2. Portion of whole sample used for LC, actual mg
3. Quantity recovered from LC column, actual mg
4. Total mg computed back to total sample

*N/A = Not Applicable

TABLE 30

IR REPORTS: FUEL OIL FRACTIONS LC 1, LC 2

IR REPORT

SAMPLE: #4 Fuel Oil, LC Fraction 1

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3000-2800	S	Aliphatic CH-CH_3	
1460, 1370	M	Aliphatic CH_3	
720	W	Long CH_2 Chain	

IR REPORT

SAMPLE: #4 Fuel Oil, LC Fraction 2

Wave Number (cm^{-1})	Intensity	Assignment	Comments
2100-3000	W	Aromatic CH	
3000-2800	S	Aliphatic CH	
1600, 1500	W	Aromatic CH	
1460, 1370	M	Aliphatic CH	
820, 750	W	Aromatic Substitution	

TABLE 31

IR REPORTS: FUEL OIL FRACTIONS LC 3, LC 4

IR REPORT

SAMPLE: #4 Fuel Oil, LC Fraction 3

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3100-3000	M	Aromatic CH	
3000-2800	S	Aliphatic CH	
1600, 1500	M	Aromatic CH	
1450, 1370	M	Aliphatic CH	
1020	W	Aromatic Substitution	
860, 810, 750	M	Aromatic Substitution	

IR REPORT

SAMPLE: #4 Fuel Oil, LC Fraction 4

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3500-3400	W	OH or NH, Broad	
3100-2700	W	OH Broad	
3050	W	Aromatic CH	
3000-2800	S	Aliphatic CH	
1700	W	Acid C = O	
1620, 1300	W	$N-NO_2$, NH_2	
1450, 1370	M	Aliphatic CH	
1230	W	Amino, Nitro, Ether	
1020	W	Ether, Alcohol, Si-O	
850, 800, 750	W	Aromatic Substitution	

TABLE 32

IR REPORTS: FUEL OIL FRACTIONS LC 5, LC 6

IR REPORT

SAMPLE: #4 Fuel Oil, LC Fraction 5

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3600–3200	W	OH	
3200–2700	W	OH, Acid	
3000–2800	S	Aliphatic CH	
1460, 1370	M	Aliphatic CH	
1150, 1020	W	Alcohol, Ester	
720	M	Long CH_2 Chain	

IR REPORT

SAMPLE: #4 Fuel Oil, LC Fraction 6

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3600–2700	W	OH	
3000–2800	S	Aliphatic CH	
1700, 1600	W	Carbonyl, Ketone, Acid	
1460, 1370	M	Aliphatic CH	
1020	M	Alcohol, Si-O	
750	M	C-Cl	

TABLE 33

IR REPORT: FUEL OIL FRACTION LC 7

IR REPORT

SAMPLE: #4 Fuel Oil, LC Fraction 7

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3600-2700	W	OH	
3000-2800	S	Aliphatic CH	
1700, 1600	W	C = O, Acid, Ketone	
1460, 1370	M	Aliphatic CH	
1020	W	Alcohol, Si-O	
750	VW	C-Cl	

IR REPORT

SAMPLE:

Wave Number (cm^{-1})	Intensity	Assignment	Comments

TABLE 34

LRMS REPORT: FUEL OIL FRACTION LC 1

LRMS REPORT

SAMPLE: #4 Fuel Oil, LC Fraction 1

Major Categories

Intensity	Category	MW Range
100	Aliphatic Hydrocarbons	170-632

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
100	Saturated Aliphatic HCs	170-632	$C_{12}H_{26}$ to $C_{45}H_{92}$
100	Unsaturated Aliphatic HCs	180-278	$C_{13}H_{24}-C_{20}H_{38}$

Other

TABLE 35

LRMS REPORT: FUEL OIL FRACTION LC 2

LRMS REPORT

SAMPLE: #4 Fuel Oil, LC Fraction 2

Major Categories

Intensity	Category	MW Range
10	Aromatic Hydrocarbons	106-624
10	Cyclic Aliphatic Hydrocarbons	to 631

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
10	Alkyl Benzenes	106-624	C_8H_{10} to $C_{45}H_{84}$
10	Pentacycloparaffins	to 440	to $C_{32}H_{56}$

Other

TABLE 36

LRMS REPORT: FUEL OIL FRACTION LC 3

LRMS REPORT

SAMPLE: #4 Fuel Oil, LC Fraction 3

Major Categories

Intensity	Category	MW Range
100	Aromatic Hydrocarbons	92-190
100	Fused Aromatic Hydrocarbons, < 216	142-198
10	Fused Aromatic Hydrocarbons, > 216	252-400

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
100	Alkyl Benzenes	92-190	C_7H_8- $C_{14}H_{22}$
100	Alkyl Naphthalenes	128-268	$C_{10}H_8$- $C_{20}H_{28}$
10	Alkyl Anthracenes/Phenanthrenes	252-400	$C_{20}H_{12}$

Other

TABLE 37

LRMS REPORT: FUEL OIL FRACTION LC 4

LRMS REPORT

SAMPLE: #4 Fuel Oil, LC Fraction 4

Major Categories

Intensity	Category	MW Range
10	Heterocyclic Nitrogen Compounds	
1	Esters	

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
10	Carbazoles	167	$C_{12}H_9N$
10	Benzocarbazoles	217	$C_{16}H_{11}N$
10	Alkylated Carbazoles	223	$C_{16}H_{17}N$
1	Phthalates		

Other

TABLE 38

LRMS REPORT: FUEL OIL FRACTION LC 6

LRMS REPORT

SAMPLE: #4 Fuel Oil, LC Fraction 6

Major Categories

Intensity	Category	MW Range
1	Carboxylic Acids	256-284
1	Esters	
1	Chlorinated Hydrocarbons	172-250

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
1	Palmitic Acid	256	$C_{16}H_{32}O_2$
1	Stearic Acid	284	$C_{18}H_{36}O_2$
1	Chlorinated Hydrocarbons*	172	
1	Chlorinated Hydrocarbons*	250	
1	Dioctyl Phthalates		

Other

*Probably contaminants introduced during sample handling.

TABLE 39

LRMS REPORT: FUEL OIL FRACTION LC 7

LRMS REPORT

SAMPLE: #4 Fuel Oil, LC Fraction 7

Major Categories

Intensity	Category	MW Range
1	Carboxylic Acid	122-284
1	Esters	

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
1	Benzoic Acid	122	$C_7H_6O_2$
1	Stearic Acid	284	$C_{18}H_{26}O_2$
1	Dioctyl Phthalate		

Other

scheme. A positive finding of these species in the later fractions only, with no indication of their presence in the more probable fractions, is a strong evidence that these are spurious results due to contaminants. The fatty acids and phthalates reported in Tables 38 and 39 may also be contaminants. However, since these species would be expected to be most abundant in LC 6 and LC 7 where they are, in fact, found, there is no basis for rejecting them as possible sample components. The carboxylic acids, therefore, are reported in the summary table (Table 28).

D. Level 1 Organic Analysis Results for a Coal Sample

The results of the application of Level 1 organic analysis procedures to a coal sample are presented in Table 40. These data were obtained by analysis of a methylene chloride extract prepared by 24-hour Soxhlet extraction of a 26.3 g sample of coal that had been ground and sieved to pass a 60 mesh screen. Less than 1% of the mass of the coal, 3500 mg/Kg, was extracted. Of the extracted material, approximately 22% was TCO range and 78% was GRAV range material; this is a higher level of volatile material than might have been expected.

Analysis of the composition of the extract showed the predominant species to be the lower molecular weight (m/e > 216) fused aromatic hydrocarbons (36% of the total sample after LC separation). Heterocyclic nitrogen compounds accounted for 22% of the total, and phenols another 21%. High molecular weight fused aromatic hydrocarbons (m/e > 216) comprised only 5% of the sample and although LRMS analysis detected elemental sulfur in LC fraction #1, no organosulfur species were detected.

Tables 41 through 52 show the results of the LC, IR and LRMS analyses that were integrated in constructing Table 40. The LC report, Table 41 shows that 80% of the GRAV range material, but only 39% of the TCO range material, was recovered from the LC column. The overall sample recovery was 70%. The "TOTAL" values in Table 41 have not been corrected by this recovery factor; the only correction applied is the factor of 2.7 reflecting

TABLE 40

ORGANIC EXTRACT SUMMARY TABLE FOR COAL SAMPLE

Sample CH_2Cl_2 extract of 26.3 g coal

	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total Organics, mg /Kg	200	72	990	270	99	240	600	2500
TCO, mg	-	0.3	6.9	2.5	-	-	-	9.7
GRAV, mg	5.3	1.6	19	4.7	2.6	6.3	16	55

Category	**Assigned Intensity MG/**							
Aliphatic Hydrocarbons	10/100	100/71						170
Sulfur	10/100	1/1						100
Fused Aromatics < 216			100/900					900
Fused Aromatics > 216			10/90		10/33			120
Heterocyclic N Compounds				10/245	10/33		10/270	550
Phenols						10/240	10/270	510
Carboxylic Acids							1/27	27

TABLE 41

LC REPORT FOR COAL EXTRACT

SAMPLE: CH_2Cl_2 Extract from 26.3 g Coal

	TCO mg	GRAV mg	TCO + GRAV Total mg	Concentration mg/ (m^3, L, or kg)
Total Sample[1]	20	72.5	92.5	3500 mg/Kg
Taken for LC[2]	9.0	26.1	35.1	
Recovered[3]	3.5	20.9	24.4	

Fraction	TCO in mg				GRAV in mg				TCO + GRAV Total mg	Concentration mg/ (m^3, L, kg)
	Found in Fraction	Blank	Cor-rected	Total[4]	Found in Fraction	Blank	Cor-rected	Total[4]		
1	–	–		–	2.0	–	2.0	5.3	5.3	200 mg/Kg
2	0.1	–	0.1	0.3	0.6	–	0.6	1.6	1.9	72
3	2.5	–	2.5	6.9	7.2	–	7.2	19.	26.	990
4	0.2	–	0.2	2.5	1.8	–	1.8	4.7	7.2	270
5	–	–		–	1.0	–	1.0	2.6	2.6	99
6	–	–		–	2.4	–	2.4	6.3	6.3	240
7	–	–		–	6.8	0.9	5.9	16.	16.	600
Sum	3.5	–	3.5	9.7	21.8	0.9	20.9	55.	65.	2500

1. Quantity in entire sample, determined before LC
2. Portion of whole sample used for LC, actual mg
3. Quantity recovered from LC column, actual mg
4. Total mg computed back to total sample

TABLE 42

IR REPORTS: COAL EXTRACT LC 1, LC 2

IR REPORT

SAMPLE: Coal Extract, LC Fraction 1

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3400	W	OH/very broad	
3000-2800	S	Aliphatic CH	
1460	S	Aliphatic CH	
1380	M	Aliphatic CH	
730, 720	M	Doublet CH_2 chain longer than 4 units	

IR REPORT

SAMPLE: Coal Extract, LC Fraction 2

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3400	W	OH or NH/broad	
3000-2800	S	Aliphatic CH, unsaturated CH	
1460	M	Aliphatic CH	
1380	W	Aliphatic CH	
720	W	Aliphatic CH, CH_2 rock	

TABLE 43

IR REPORTS: COAL EXTRACT LC 3, LC 4

IR REPORT

SAMPLE: Coal Extract, LC Fraction 3

Wave Number (cm⁻¹)	Intensity	Assignment	Comments
3080-3000	M	Aromatic CH	
3000-2800	S	Aliphatic CH	
1600	M	Aromatic ring	
1450	S	Aliphatic CH	
1370	M	Aliphatic CH	
870, 805, 740	M	Aromatic substitution	

IR REPORT

SAMPLE: Coal Extract, LC Fraction 4

Wave Number (cm⁻¹)	Intensity	Assignment	Comments
3420	W	OH or NH/broad	
3080-3000	W	Aromatic CH	
3000-2800	S	Aliphatic CH	
1600	W	Aromatic ring, amine, nitroso	
1450	M	Aliphatic CH	
1370	W	Aliphatic CH	
870, 800, 740	W	Aromatic substitution	

TABLE 44

IR REPORTS: COAL EXTRACT LC 5, LC 6

IR REPORT

SAMPLE: Coal Extract, LC 5

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3400	W	OH or NH/broad	
3080-3000	W	Aromatic CH	
3000-2800	S	Aliphatic CH	
1700	W	Acid, ketone	
1600	W	Aromatic ring, amine, nitroso	
1460	M	Aliphatic CH	
1370	W	Aliphatic CH	
750	W	Aromatic substitution NH_2	

IR REPORT

SAMPLE: Coal Extract, LC 6

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3300	M	OH or NH/broad	
3080-3000	W	Aromatic CH	
3000-2800	S	Aliphatic CH	
1690,1650,1600	M	Acid, ketone, amine	
1450	M	Aliphatic CH, nitrosamine	
1220	W	Ether, phenol	
1050	W	Alcohol	
880, 820, 750	S	Aromatic substitution	

TABLE 45

IR REPORT: COAL EXTRACT LC 7

IR REPORT

SAMPLE: Coal Extract, LC Fraction 7

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3350	M	OH or NH/broad	
3000-2800	S	Aliphatic CH	
1730	M	Ester	
1650, 1610	M	Ketone, acid, amine	
1460	M	Aliphatic CH	
1370	M	Aliphatic CH	
1280, 1220	M	Ester, ether, alcohol	
1150	M	Ether, alcohol, ester	
1020	W	Alcohol, acid	
750	W	Aromatic substitution	

IR REPORT

SAMPLE:

Wave Number (cm^{-1})	Intensity	Assignment	Comments

TABLE 46

LRMS REPORT: COAL EXTRACT LC 1

LRMS REPORT

SAMPLE: Coal Extract, LC Fraction 1

Major Categories

Intensity	Category	MW Range
10	Aliphatic hydrocarbons	212-482
10	Sulfur	256

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
10	Saturated aliphatic hydrocarbons	212 to	$C_{15}H_{32}$ to
		422	$C_{30}H_{62}$
10	Unsaturated aliphatic hydrocarbons	398 to	$C_{29}H_{50}$ to
		482	$C_{35}H_{62}$
10	Sulfur	256	S_8

Other

TABLE 47

LRMS REPORT: COAL EXTRACT LC 2

LRMS REPORT

SAMPLE: Coal Extract, LC Fraction 2

Major Categories

Intensity	Category	MW Range
100	Aliphatic hydrocarbons	170-422
1	Sulfur	256

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
10	Saturated aliphatic hydrocarbons	170 to	$C_{12}H_{26}$ to
		422	$C_{30}H_{62}$
10	Unsaturated aliphatic hydrocarbons	182 to	$C_{13}H_{26}$ to
		420	$C_{30}H_{60}$
10	Unsaturated aliphatic hydrocarbons	180 to	$C_{13}H_{24}$ to
		418	$C_{30}H_{58}$
10	Unsaturated aliphatic hydrocarbons	178 to	$C_{13}H_{22}$ to
		416	$C_{30}H_{56}$
10	Unsaturated aliphatic hydrocarbons	176 to	$C_{13}H_{20}$ to
		414	$C_{30}H_{54}$
10	Unsaturated aliphatic hydrocarbons	174 to	$C_{13}H_{18}$ to
		412	$C_{30}H_{52}$
1	Sulfur	256	S_8

Other

TABLE 48

LRMS REPORT: COAL EXTRACT LC 3

LRMS REPORT

SAMPLE: Coal Extract, LC Fraction 3

Major Categories

Intensity	Category	MW Range
100	Fused aromatic hydrocarbons, m/e < 216	128-212
10	Fused aromatic hydrocarbons, m/e > 216	252-500

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
10	Alkyl naphthalenes	128-212	$C_{10}H_8$ - $C_{16}H_{20}$
10	Acenaphthene/biphenyl	154-210	$C_{12}H_{10}$ - $C_{16}H_{18}$
10	Anthracene/phenanthrene	178	$C_{14}H_{10}$
10	Alkylated fused aromatic hydrocarbons	252 to 500	$C_{20}H_{12}$

Other

TABLE 49

LRMS REPORT: COAL EXTRACT LC 4

LRMS REPORT

SAMPLE: Coal Extract, LC Fraction 4

Major Categories

Intensity	Category	MW Range
10	Heterocyclic nitrogen compounds	167-273
1	Esters	

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
10	Carbazole	167	$C_{12}H_9N$
10	Benzocarbazole	217	$C_{16}H_{11}N$
10	Alkylated benzocarbazoles	273	$C_{20}H_{19}N$
1	Phthalates		

Other

TABLE 50

LRMS REPORT: COAL EXTRACT LC 5

LRMS REPORT

SAMPLE: Coal Extract, LC Fraction 5

Major Categories

Intensity	Category	MW Range
10	Esters	222
10	Heterocyclic nitrogen compounds	167-223
10	Fused aromatic hydrocarbons	240-400

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
10	Diethyl phthalate	222	$C_{12}H_{14}O_4$
10	Alkyl carbazoles	167	$C_{12}H_9N$
10	Alkyl carbazoles	223	$C_{16}H_{17}N$
10	Alkyl naphthalenes	184-226	$C_{14}H_{16}$ - $C_{17}H_{22}$
10	Fused aromatic hydrocarbons, m/e > 216	240-400	

Other

TABLE 51

LRMS REPORT: COAL EXTRACT LC 6

LRMS REPORT

SAMPLE: Coal Extract, LC Fraction 6

Major Categories

Intensity	Category	MW Range
10	Phenols	108-150

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
10	Alkylated phenols	108-150	C_7H_8O - $C_{10}H_{14}O$

Other

TABLE 52

LRMS REPORT: COAL EXTRACT LC 7

LRMS REPORT

SAMPLE: Coal Extract, LC Fraction 7

Major Categories

Intensity	Category	MW Range
10	Phenols	94-178
10	Heterocyclic nitrogen compounds	145-251
1	Esters	
1	Carboxylic acids	

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
10	Alkylated phenols	94-178	C_6H_6O - $C_{12}H_{18}O$
10	Alkyl indoles	145-201	$C_{10}H_{11}N$ - $C_{14}H_{19}N$
10	Alkyl carbazoles	167-251	$C_{12}H_9N$ - $C_{18}H_{21}N$
1	Benzoic acid	122	$C_7H_6O_2$
1	Phthalate		

Other

10	Fused aromatic hydrocarbons	m/e 200-400

the fraction of the total sample (38%) taken for LC.

As in the case of the fuel oil, comparison of the IR reports (Tables 42-45) and LRMS reports (Tables 46-52) reveal no inconsistencies in the qualitative analysis results. The phthalate ester species found by LRMS probably indicates sample contamination, since the material appears to be present at equal amounts in LC 4, LC 5 and LC 7 but absent from LC 6 which is the most probable LC fraction for phthalate ester elution. The phthalate esters are, therefore, not reported in Table 40.

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XI. EXAMPLE OF APPLICATION OF LEVEL 1 PROCEDURES TO A SASS TRAIN SAMPLE

A. Introduction

This chapter presents an example of application of Level 1 organic analysis procedures to a sample of gaseous effluent from a sealed metallurgical furnace at a ferroalloy production facility. The sample was collected by personnel of Monsanto Research Corporation using the IERL Source Assessment Sampling System (SASS train) (1) and was sent to Arthur D. Little, Inc., for analysis. A report of the complete study has been published (9).

B. Summary of Level 1 Results

Data on the total extractable organic material for the various SASS train components for this ferromanganese process sample are summarized in Table 53. Substantial amounts of organic matter were found in the extracts of all SASS train components, except the sorbent condensate extract, from the ferromanganese process. About 92% of the material was found in the XAD-2 extract in this case, of which about 82% was found to be high-boiling (b.p. >300°C) material.

The extracts containing more than 0.5 mg/m^3 of total organic material were taken through LC separations, and the seven LC fractions collected from each extract were analyzed for TCO and GRAV as well as by IR and LRMS. Tables 54-56 are organic extract summary tables for the probe wash, fine particulate fraction and sorbent module portions of this SASS sample and Table 57 presents the overall organic summary for the ferroalloy process stream sampled.

10 Lines to End of Typing Area

Some interesting aspects of these data are:

> Extremely high quantities of fused aromatics (Table 56) over all molecular weight ranges were found in the XAD-2 module extract including many non-volatile species. Also present in this sample were:

For Page Numbering

TABLE 53

TOTAL EXTRACTABLE ORGANICS FOR SASS TRAIN SAMPLES OF FERROMANGANESE PROCESS EMISSIONS, mg/m^3

	TCO	GRAV	TOTAL
Particulate extracts			
10 + 3μm	--	6.6	6.6
1μ + filter	--	48.	48.
probe and cyclone rinse extract	--	37.	37.
XAD-2 extract	205	910	1100
Sorbent condensate extract	0.41	∿0.1	0.41

Source: Reference 9

TABLE 54

ORGANIC EXTRACT SUMMARY TABLE: FERROMANGANESE PROCESS SASS CONDENSATE

Sample II PW, Probe Wash, Ferromanganese

	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total Organics, mg/m^3	1.95	<0.1	28	7.8	0.54	7.2	1.44	47
TCO, mg	-	-	-	-	-	-	-	-
GRAV, mg	2.65	<0.1	39	11	0.73	9.8	1.96	65

Category	Int/mg/m^3							
Aliphatic Hydrocarbons	1/1.9							1.9
Aromatic Hydrocarbons		<<0.2						<<0.2
Fused Aromatics <216			100/14	1/0.07				14.
Fused Aromatics >216			100/14	100/7.7	100/0.2*			22
Heterocyclic N compounds				1/0.07		10/0.6	1/0.1	0.8
Ketones (polycyclic aromatic)					100/0.2*	100/6.5	10/1.3	7.8
Esters					10/0.02*	1/0.06		0.08
Alcohols					10/0.02*			0.02
Nitrile					10/0.02*			0.02

*Concentration estimated from LC, IR data with reference to LRMS data of LC4 and LC6

TABLE 55

ORGANIC EXTRACT SUMMARY TABLE

Sample IICIF, Particulates <1μ, Ferromanganese

	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total Organics, mg/m^3	<0.1	<0.1	23	10	<0.1	13	1.5	48
TCO, mg	–	–	–	–	–	–	–	–
GRAV, mg	<0.1	<0.1	32	14	<0.1	18	2.0	66

Category	Int/mg/m^3							
Aliphatic Hydrocarbons	<<0.2							<<0.2
Aromatic Hydrocarbons		<<0.2						<<0.2
Fused Aromatics <216			1/0.2					0.2
Fused Aromatics >216			100/23	10/10	<<0.2			33
Ketones (polycyclic aromatic)					<<0.2	100/6.4		6.4
Heterocyclic N compounds						100/6.4	1/1.5	7.9
Esters						1/0.06		0.06
Carboxylic Acids						1/0.06		0.06

TABLE 56

ORGANIC EXTRACT SUMMARY TABLE

Sample IIX, XAD-2 Extract, Ferromanganese

	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total Organics, mg/m^3	3.9	7.0	780	36.	6.7	88	17	940
TCO, mg	2.25	9.4	195	1.21	6.2	30	11	255
GRAV, mg	3.0	<0.1	870	48.	3.0	90	12	940

Category	Int/mg/m^3							
Aliphatic Hydrocarbons	100/3.9							3.9
Aromatic Hydrocarbons		10/3.5						3.5
Fused Aromatics <216		10/3.5	100/372	10/1.7				380
Fused Aromatics >216			100/372	100/17				390
Heterocyclic S compounds			10/37					37
Heterocyclic N compounds				100/17	100/3.2	100/42	10/8.1	70
Ketones (polycyclic aromatic)					100/3.2	100/42	10/8.1	53
Nitriles					10/0.3			0.3
Carboxylic acids						10/4.2		4.2
Esters							1/0.8	0.8

TABLE 57

TOTAL ORGANICS (mg/m^3) FOR SASS TRAIN SAMPLES OF FERROMANGANESE PROCESS EFFLUENT

Compound Categories	Particulates			Sorbent Module		Total
	>3µ*	<3µ	Rinses	Resin	Condens.*	
Aliphatic Hydrocarbons		∿0.1	1.9	3.9		6.9
Aromatic Hydrocarbons		∿0.1	∿0.1	3.5		3.7
Fused Aromatics <216		0.2	14	370		380
Fused Aromatics >216	4.5	33	22	390	0.3	450
Heterocyclic S				37		37
Heterocyclic N	1.1	7.9	0.8	70	0.07	80
Ketones	0.8	6.4	7.8	53	0.05	67
Alcohols			0.02			∿0.1
Nitriles			0.02	0.3		0.3
Esters		0.06	0.08	0.8		0.9
Carboxylic Acids		0.06		4.2		4.3

*Concentrations estimated from IR and total TCO and Grav data only.

SOURCE: Reference 9.

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heterocyclic nitrogen and sulfur compounds, polycyclic aromatic ketones, and trace amounts of nitriles and esters. The LC separations between aromatic and polar species were very good.

The most abundant organic species present in the particulate extracts (Tables 54 and 55) were similar to those found in the XAD-2 extract (II X), i.e., fused aromatics in LC 3 and heterocyclic nitrogen compounds and ketones in LC 6.

The extracts that had insufficient organic material for LC separations and subsequent analysis were examined by infrared only. By combining the IR data with the TCO and GRAV results, the organic materials in each extract were very roughly categorized and approximate concentrations estimated. These data, along with the data in Tables 54-56 were integrated to constuct summary tables describing the concentration distribution of compound categories from each SASS train (Table 57).

C. Detailed Level 1 Results

The LC, IR and LRMS results for the ferromanganese process effluent SASS sample are presented in Tables 58-68 for the Probe Wash/Rinse extract and in Tables 69-80 for the XAD-2 sorbent trap extract.

TABLE 58 LC REPORT: FERROMANGANESE PROBE WASH SAMPLE

SAMPLE: II PW, PROBE WASH, FERROMANGANESE

	TCO mg	GRAV mg	TCO + GRAV Total mg	Concentration mg/ (m^3, L, or kg)
Total Sample[1]	---	51	51	37
Taken for LC[2]	---	25	25	
Recovered[3]	---	32	32	

Fraction	TCO in mg				GRAV in mg				TCO + GRAV Total mg	Concentration mg/ (m^3, L, kg)
	Found in Fraction	Blank	Cor-rected	Total[4]	Found in Fraction	Blank	Cor-rected	Total[4]		
1				---				2.65	2.65	1.95
2				---				ND[6]	ND	ND
3				---				39	39	28
4				---				11	11	7.84
5				---				0.73	0.73	0.54
6				---				9.81	9.81	7.21
7				---				1.96	1.96	1.44
Sum										

1. Quantity in entire sample, determined before LC
2. Portion of whole sample used for LC, actual mg
3. Quantity recovered from LC column, actual mg
4. Total mg computed back to total sample
5. Total mg divided by total volume
6. Not detectable

TABLE 59 IR REPORT: FERROMANGANESE PROBE WASH LC1, LC2

SAMPLE: II PW-1, LC1, Probe Wash, Ferromanganese

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3000-2800	S	CH, aliphatic	
1500-1300	SM	CH, aliphatic	

IR REPORT

SAMPLE: II PW-2, LC2, Probe Wash, Ferromanganese

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3000-2800	W	CH, aliphatic	

TABLE 60 IR REPORT: FERROMANGANESE PROBE WASH LC3, LC4

SAMPLE: II PW-3, LC3, Probe Wash, Ferromanganese

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3100-3000	S	CH, aromatic olefinic	
1930	W	$C=C=CH_2$ allene	
3000-2800	W	CH, aliphatic	
1600-1000	M	numerous sharp bands	
		aromatic ring	
900-700	S	multiple bands, aromatic	
		substitution, fused rings	

IR REPORT

SAMPLE: II PW-4, LC4, Probe Wash, Ferromanganese

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3500-3200	W	NH or OH	
3100-3000	M	CH, aromatic, olefinic	
3000-2800	W	CH, aliphatic	
1600	M	C=C, aromatic ring	
1500-1000	M-W	multiple bands, aromatic ring	
900-700	S	aromatic substitution	

TABLE 61 IR REPORT: FERROMANGANESE PROBE WASH, LC5, LC6

SAMPLE: II PW-5, LC5, Probe Wash, Ferromanganese

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3500-3200	M	OH, NH	
3100-3000	M	CH, aromatic, olefinic	
3000-2800	S	CH, aliphatic	
2210	W	C≡N, nitrile	
1730	M	C=0, ester	
1700	S	C=0, ketone, acid, carbamate	
		imide, cyclic imide	
1650	W	C=C	
1600, 1580	M	aromatic substitution	
1450, 1350		amines	
1520, 1350	M	nitro aromatic	
1280, 1120	W	aromatic ester	
820, 750	S	aromatic substitution	

SAMPLE: II PW-6, LC6, Probe Wash, Ferromanganese

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3500-3200	W	OH, NH	
3100-3000	M	CH, aromatic, olefinic	
3000-2800	S	CH, aliphatic	
1720	S	C=O, ester	
1700	S	C=0, acid, ketone	
1660, 1620	S	amide, nitrite	
1580, 1300	S	$N-NO_2$, nitramine	
1270, 1120	S	aromatic ester	
1230, 1210	S	ester	
1180, 1060		alcohol	
750	S	aromatic substitution, C-Cl	

TABLE 62 IR REPORT: FERROMANGANESE PROBE WASH, LC7

SAMPLE: II PW-7, Probe Wash, Ferromanganese

Wave Number (cm⁻¹)	Intensity	Assignment	Comments
3700-3100	S	OH or NH, broad	
3100-3000	W	CH, aromatic	
3000-2800	SM	CH, aliphatic	
30007-22400	W	OH, acid, broad	
1720	S	C=O, ester, ketone	
1670,1640,1600	S	ketone, amide, amidine, nitrite	
		nitrate	
1250	S	ester, phosphate, P=N cyclic	
		CF_3, C-Cl, Si-CH_3	
1060, 1000	M	alcohol	
750	S	aromatic subst, PF, CF_3, C-Cl	

SAMPLE:

Wave Number (cm⁻¹)	Intensity	Assignment	Comments

TABLE 63 LRMS REPORT: FERROMANGANESE PROBE WASH, LC1

SAMPLE: Monsanto Ferro Alloy, II PW-1

Major Categories

Intensity	Category	MW Range
1	Aliphatics	200-450

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition

Other

1	aliphatics with $200 \leq m/e < 450$

TABLE 64 LRMS REPORT: FERROMANGANESE PROBE WASH, LC2

SAMPLE: Monsanto Ferro Alloy, II PW-2

Major Categories

Intensity	Category	MW Range
10	aromatic hydrocarbons	225

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition

Other

10	benzene substituted with aliphatic chain and N and Cl
	exterior to ring with m/e = 225 ($C_{13}H_{20}NCl$)

TABLE 65 LRMS REPORT: FERROMANGANESE PROBE WASH, LC3

SAMPLE: Monsanto Ferro Alloy, II PW-3

Major Categories

Intensity	Category	MW Range
100	fused alternate/non-alternate hydrocarbons	<216
100	fused alternate/non-alternate hydrocarbons	>216

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
100	pyrene/fluoranthene	202	$C_{16}H_{10}$
100	benzoanthracene, etc.	228	$C_{18}H_{12}$
100	benzopyrenes, etc.	252	$C_{20}H_{12}$
10	anthracene/phenanthrene	178	$C_{14}H_{10}$
10	benzofluorene, etc.	216	$C_{17}H_{12}$
10		218	$C_{17}H_{14}$
10	methyl-benzanthracene	242	$C_{19}H_{14}$
10	dibenzchrysene	276	$C_{22}H_{12}$
10	dibenzanthracene	278	$C_{22}H_{14}$
10	dibenzepyrene	302	$C_{24}H_{14}$
10		326	

Other

1	polycyclics with 326 < m/e ≤450

TABLE 66 LRMS REPORT: FERROMANGANESE PROBE WASH, LC4

SAMPLE: Monsanto Ferro Alloy, II PW-4

Major Categories

Intensity	Category	MW Range
100	fused alternate/non-alternate hydrocarbons	<216
1	fused alternate/non-alternate hydrocarbons	>216
1	heterocyclic nitrogen compounds	217

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
100	chrysene/benzanthracene	228	$C_{18}H_{12}$
100	benzopyrene, etc.	252	$C_{20}H_{12}$
10	dibenzchrysene	276	$C_{22}H_{12}$
10	dibenzanthracene	278	$C_{22}H_{14}$
10	dibenzpyrene	302	$C_{24}H_{14}$
10		326	
1	benzocarbazole	217	$C_{16}H_{11}N$
1		242	$C_{19}H_{14}$
1		258	
1	pyrene/fluoranthene	202	$C_{16}H_{10}$
1		376	

Other

<1	polycyclics below 200
1	polycyclics 380 $\leq$ m/e $\leq$460

TABLE 67 LRMS REPORT: FERROMANGANESE PROBE WASH, LC6

SAMPLE: Monsanto Ferro Alloy, II PW-6

Major Categories

Intensity	Category	MW Range
100	ketones	300+
10	heterocyclic nitrogen compounds	200-300+
1	esters	

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
100	benzanthrone, etc.	230	$C_{17}H_{10}O$
10	phthalate		
10		200	
10		202	
10		203	$C_{15}H_9N$
10		243	
10		244	
10	5 ring-N	253	$C_{19}H_{11}N$
10	5 ring-O (polycyclic aromatic ketone)	254	$C_{19}H_{10}O$
10		258	
10	dibenzacridine, etc.	279	$C_{21}H_{13}N$
10		280	
10		302	
10	6-ring N	303	
10	6-ring O (ketone on 6-fused rings)	304	
1	fluorenone, etc.	180	$C_{13}H_8O$

Other

1 polycyclics with 305 $\leq$ m/e <460

TABLE 68 LRMS REPORT: FERROMANGANESE PROBE WASH, LC7

SAMPLE: Monsanto Ferro Alloy, II PW-7

Major Categories

Intensity	Category	MW Range
10	ketones	200-300+
1	heterocyclic nitrogen compounds	179-300+

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
10	benzanthrone, etc.	230	$C_{17}H_{10}O$
1	acridine	179	$C_{13}H_9N$
1		203	$C_{15}H_9N$
1		204	
1		229	$C_{17}H_{11}N$
1		253	$C_{19}H_{11}N$
1		254	
1		279	$C_{21}H_{13}N$
1		280	
1	6-ring N	303	
1		304	

Other

1 polycyclics up to m/e 350

TABLE 69 LC REPORT: FERROMANGANESE XAD-2 SORBENT TRAP SAMPLE

SAMPLE:

	TCO mg	GRAV mg	TCO + GRAV Total mg	Concentration mg/ (m^3, L, or kg)
Total Sample[1]	279	1230	1510	1110
Taken for LC[2]	18.6	74.2	92.8	
Recovered[3]	17.0	68.2	85.2	

Fraction	TCO in mg				GRAV in mg				TCO + GRAV Total mg	Concentration mg/ (m^3, L, kg)
	Found in Fraction	Blank	Cor-rected	Total[4]	Found in Fraction	Blank	Cor-rected	Total[4]		
1				2.25				3.0	5.25	3.86
2				9.45				ND[6]	9.45	6.95
3				195				867	1062	781
4				1.21				48	49	36
5				6.15				3.0	9.15	6.73
6				29.7				90	120	88
7				11				12	23	17
Sum										

1. Quantity in entire sample, determined before LC
2. Portion of whole sample used for LC, actual mg
3. Quantity recovered from LC column, actual mg
4. Total mg computed back to total sample
5. Total mg divided by total volume
6. Not detectable.

TABLE 70 IR REPORT: FERROMANGANESE XAD-2 SAMPLE, LC1, LC2

SAMPLE: II X-1, LC1, XAD Extract, Ferro Alloy

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3000-2800	S	CH, aliphatic	
1500-1350	M	CH, aliphatic	

SAMPLE: II X-2, LC2, XAD Extract, Ferromanganese

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3000-2800	S	CH, aliphatic	
1500-1350	M	CH, aliphatic	

TABLE 71 IR REPORTS: FERROMANGANESE XAD-2 SAMPLE, LC3, LC4

SAMPLE: II X-3, LC3, XAD Extract, Ferromanganese

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3100-3000	S	CH, aromatic, olefinic	
1600-1050	M,W	numerous sharp bands, aromatic	
900-700	S	numerous sharp bands, aromatic	
		rings, fused rings	

SAMPLE: II X-4, LC4, XAD Extract, Ferromanganese

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3400	S	NH or OH	
3100-3000	W	CH, aromatic	
1600, 1500	M	aromatic ring	
1320(d)	M	C-N	
1240	M	aromatic H rocking	
800, 750	S	aromatic subst.	
720		fused rings	
x positive identification of		carbazole	

TABLE 72 IR REPORT: FERROMANGANESE XAD-2 SAMPLE, LC5, LC6

SAMPLE: II X-5, LC5, XAD Extract, Ferromanganese

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3400	W	NH or OH	
3050	W	CH, aromatic	
2220	W	C=N, N=C=0	
1700	W	C=0	
1600, 1450	W	sharp bands, aromatic ring	
750, 700	M	aromatic subst.	

SAMPLE: II X-6, LC6, XAD Extract, Ferromanganese

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3500-3100	W	OH or NH	
3100-3000	W	CH, aromatic, olefinic	
3000-2800	W	CH, aliphatic	
1710	S	C=0	
1670	W	C=C	
1600, 1500	W	aromatic ring	
1450-1100	W	aromatic ring, sharp bands	
820	W	aromatic subst.	
750, 720	S	aromatic subst.	

TABLE 73 IR REPORT: FERROMANGANESE XAD-2 SAMPLE, LC7

SAMPLE: II X-7, LC7, XAD Extract, Ferromanganese

Wave Number (cm^{-1})	Intensity	Assignment	Comments
No significant IR bands.			

SAMPLE:

Wave Number (cm^{-1})	Intensity	Assignment	Comments

TABLE 74 LRMS REPORT; FERROMANGANESE XAD-2 SAMPLE, LC1

SAMPLE: II X-1, XAD-2 Extract, Ferromanganese

Major Categories

Intensity	Category	MW Range
100	aliphatic hydrocarbons	200-480

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition

Other

TABLE 75 LRMS REPORT: FERROMANGANESE XAD-2 SAMPLE, LC2

SAMPLE: II X-2, XAD-2 Extract, Ferromanganese

Major Categories

Intensity	Category	MW Range
10	alkylated polycyclics or aromatics	200-380
10	fused aromatics <216	202

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
10	pyrene	202	$C_{16}H_{10}$

Other

TABLE 76 LRMS REPORT: FERROMANGANESE XAD-2 SAMPLE, LC3

SAMPLE: II X-3, XAD-2 Extract, Ferromanganese

Major Categories

Intensity	Category	MW Range
100	fused aromatics <216	152-210
100	fused aromatics >216	216-350
10	heterocyclic S compds.	184

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
100	anthracene/phenanthrene	178	$C_{14}H_{10}$
100	pyrene/fluoranthene	202	$C_{16}H_{10}$
100	chrysene, benzanthracenes	228	$C_{18}H_{12}$
100	benzopyrene, perylene	252	$C_{20}H_{12}$
10	acenaphthylene	152	$C_{12}H_8$
10	fluorene	166	$C_{13}H_{10}$
10	methyl acenaphthalene	168	$C_{13}H_{12}$
10	dibenzthiophene	184	$C_{12}H_8S$
10	methyl anthracene	192	$C_{15}H_{12}$
10	benzofluorenes	216	$C_{17}H_{12}$
10	benzonaphthalene	218	$C_{17}H_{14}$

Other

10	PAH at m/e 230-302
1	PAH at m/e 190-350

TABLE 77 LRMS REPORT: FERROMANGANESE XAD-2 SAMPLE, LC4

SAMPLE: II X-4, XAD-2 Extract, Ferromanganese

Major Categories

Intensity	Category	MW Range
100	heterocyclic N compds.	167-267
100	fused aromatics 216	228-302
10	fused aromatics 216	178-202

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
100	carbazole	167	$C_{13}H_9N$
100	benzocarbazole	217	$C_{16}H_{11}N$
100	benzopyrenes	252	$C_{20}H_{12}$
10	anthracene/phenanthrene	178	$C_{14}H_{10}$
10	methyl carbazole	181	$C_{14}H_{11}N$
10	dimethyl carbazole	195	$C_{15}H_{13}N$
10	pyrene	202	$C_{16}H_{10}$
10	benzoanthracenes, chrysene	228	$C_{18}H_{12}$
10	methyl benzocarbazole	231	$C_{17}H_{13}N$
10	dibenzocarbazole	267	$C_{20}H_{13}N$
10	benzoperylene	276	$C_{22}H_{12}$
10	methyl cholanthrene	268	$C_{21}H_{16}$
10	dibenzochrysenes	302	$C_{22}H_{14}$

Other

10	PAH at m/e 191, 241, 243, 245, 257, 258, 326
1	PAH at m/e 200 to over 400

TABLE 78 LRMS REPORT: FERROMANGANESE XAD-2 SAMPLE, LC5

SAMPLE: II X-5, XAD-2 Extract, Ferromanganese

Major Categories

Intensity	Category	MW Range
100	heterocyclic N compds.	167-253
100	ketones	230-280
10	nitriles	153

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
100	carbazole	167	$C_{12}H_9N$
100	benzanthrone	230	$C_{17}H_{10}O$
10	naphthalenecarbonitrile	153	$C_{11}H_7N$
10	methyl carbazole	181	$C_{13}H_{11}N$
10	4-ring heterocyclic N	203	$C_{15}H_9N$
10	benzocarbazole	217	$C_{16}H_{11}N$
10	4-ring N	227	$C_{17}H_9N$
10	5-ring N	253	$C_{19}H_{11}N$
10	dibenzofluorenone	280	$C_{21}H_{12}O$

Other

10	PAH at m/e 254
1	heterocyclic N, m/e 179-239
1	oxygen cmpds. m/e 180-380

TABLE 79 LRMS REPORT; FERROMANGANESE XAD-2 SAMPLE, LC6

SAMPLE: II X-6, XAD-2 Extract, Ferromanganese

Major Categories

Intensity	Category	MW Range
100	heterocyclic N compds.	179-303
100	ketones	180-304
10	carboxylic acids	122

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
100	acridine	179	$C_{13}H_9N$
100	fluorenone	180	$C_{13}H_8O$
100	4-ring heterocyclic N	203	$C_{15}H_9N$
100	4-ring heterocyclic O	204	$C_{15}H_8O$
100	anthraquinoline	229	$C_{17}H_{11}N$
100	benzanthrone	230	$C_{17}H_{10}O$
10	benzoic acid	122	$C_7H_6O_2$
10	methyl acridine	193	$C_{14}H_{11}N$
10	methyle fluorenone	194	$C_{14}H_{10}O$
10	dimethyl acridine	207	$C_{15}H_{13}N$
10	anthraquinone	208	$C_{14}H_8O_2$
10	benzocarbazole	217	$C_{16}H_{11}N$
10	methyl anthraquinoline	243	$C_{18}H_{13}N$
10	5-ring N	255	$C_{19}H_{11}N$
10	6-ring N	303	
10	dibenz acridine	279	$C_{21}H_{13}N$

Other

10	PAH at m/e 219, 244, 254, 258, 280, 304
1	PAH at m/e 265-380

TABLE 80 LRMS REPORT: FERROMANGANESE XAD-2 SAMPLE, LC7

SAMPLE: II X-7, XAD-2 Extract, Feromanganese

Major Categories

Intensity	Category	MW Range
10	heterocyclic N compds.	129-303
10	ketones	230-280
1	esters	136

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
10	acridine	179	$C_{13}H_9N$
10	4-ring N	203	$C_{15}H_9N$
10	benzocarbazole	217	$C_{16}H_{11}N$
10	benzophenanthridene	229	$C_{17}H_{11}N$
10	benzanthrone	230	$C_{17}H_{10}O$
10	5-ring heterocyclic N	253	$C_{19}H_{11}N$
10	6-ring heterocyclic N	279	$C_{21}H_{13}N$
10	dibenzofluorenone	280	$C_{21}H_{12}O$
1	quinoline	129	C_9H_7N
1	alkyl quinolines	143-171	$C_{10}H_9N$ - $C_{12}H_{13}N$
1	methyl benzoate	136	$C_8H_8O_2$
1	methyl acridine	193	$C_{14}H_{11}N$

Other

1 PAH at m/e 200-329

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XII. REFERENCES

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APPENDIX A

LEVEL 1 ORGANIC ANALYSIS TECHNIQUES

This material is reproduced exactly as it appears in the second edition of the Level 1 procedures manual (Reference 4, p. 150 of this document). Figure, Table and Reference numbers within this Appendix are those of Lentzen *et.al*. and do not correspond to those in the body of this report.

CHAPTER 9

LEVEL 1 ORGANIC ANALYSIS TECHNIQUES

9.1 INTRODUCTION

The objective of Level 1 organic analysis is to identify the major classes of organic compounds present in a process or effluent stream and to estimate their concentrations. An example of the kind of information the methodology is designed to provide is given in Table 14.

Samples obtained in accordance with the procedures outlined in Chapters 3 through 7 will be either gases, liquids, or solids. The multimedia analysis flow scheme presented in Figure 29 shows how each of the sample types is split for organic analysis.

In Level 1 organic analysis, quantitative information is provided by gas chromatography (total chromatographable organics--TCO) and by gravimetry (GRAV). Qualitative and semiquantitative information is obtained from liquid chromatography fractionation, from infrared spectra, and from low resolution mass spectra. In order to achieve a satisfactory characterization of the sample, the analyst must integrate all of these data, as well as any other available information about the source. Knowledge gained from any one part of the analysis scheme (e.g., LC separation) should be used, to the maximum extent possible, in interpreting the results from other parts (e.g., IR or LRMS spectrum). Table 15 summarizes the data expected from individual samples undergoing Level 1 organic analysis.

9.2 LEVEL 1 ORGANIC ANALYSIS METHODOLOGY (ref. 95)

An overview of the methodology to be used for the Level 1 organic analysis is shown in Figure 30. This methodology deals with the preparation of the samples to provide a form suitable for analysis, and with their subsequent analysis.

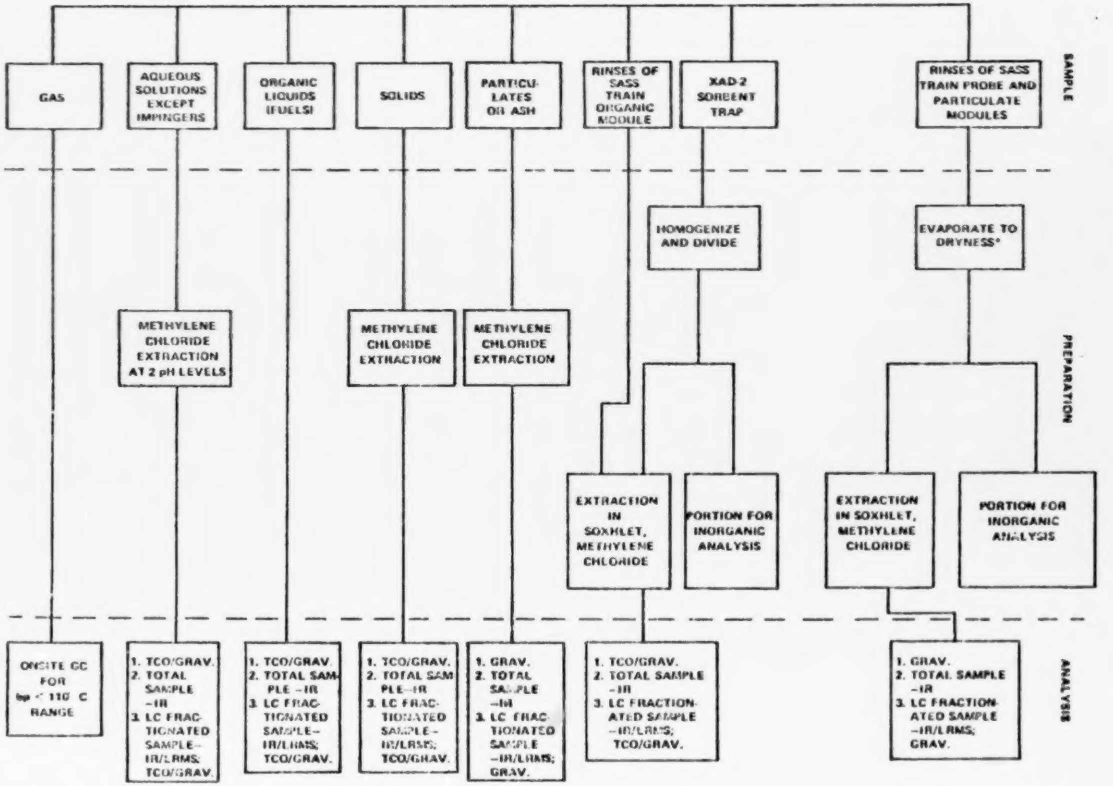
TABLE 14. SUMMARY OF RESULTS FOR ORGANIC EXTRACTS FOR SASS TRAIN SAMPLE

	$\sum$, mg/m^3						
	Particulate module			Sorbent module			
Categories	Rinses*	>3 μm	<3 μm	Resin	Rinse	Condensate†	Total‡
Aliphatic hydrocarbons		<0.06	<0.04	0.3	0.8		1.1
Aromatic hydrocarbons--benzenes				0.6			0.6
Fused aromatics, MW <216		0.25	0.15	6.3	22		29.
Fused aromatics, MW >216		0.25	0.15	4.2	21		26.
Heterocyclic N		0.31	0.19	0.6	19		20.
Heterocyclic S		<0.06	<0.04	0.4	2		2.4
Heterocyclic O		<0.06	<0.04	0.2	2		2.2
Phenols		0.06	0.04	0.1			0.2
Esters		0.18	0.11	0.1	0.1		0.5
Carboxylic acids		<0.06	<0.04	0.3	0.3		0.6
Sulfur					0.2		0.2
Inorganics				0.1			0.1
Unclassified		0.06	<0.04	0.2			0.3
Silicones		0.06	0.04				0.1

*Rinses corresponded to 0.03 mg/m^3 of organics and were not subjected to LC-IR-LRMS analysis.

†No condensate was collected for this sample.

‡Rounded results.


SAMPLE
PREPARATION
ANALYSIS
GAS
AQUEOUS SOLUTIONS EXCEPT IMPINGERS
ORGANIC LIQUIDS (FUELS)
SOLIDS
PARTICULATES OR ASH
RINSES OF SASS TRAIN ORGANIC MODULE
XAD-2 SORBENT TRAP
RINSES OF SASS TRAIN PROBE AND PARTICULATE MODULES
HOMOGENIZE AND DIVIDE
EVAPORATE TO DRYNESS*
METHYLENE CHLORIDE EXTRACTION AT 2 pH LEVELS
METHYLENE CHLORIDE EXTRACTION
METHYLENE CHLORIDE EXTRACTION
EXTRACTION IN SOXHLET, METHYLENE CHLORIDE
PORTION FOR INORGANIC ANALYSIS
EXTRACTION IN SOXHLET, METHYLENE CHLORIDE
PORTION FOR INORGANIC ANALYSIS
ONSITE GC FOR bp < 110° C RANGE
1. TCO/GRAV. 2. TOTAL SAMPLE –IR 3. LC FRACTIONATED SAMPLE–IR/LRMS; TCO/GRAV.
1. TCO/GRAV. 2. TOTAL SAMPLE –IR 3. LC FRACTIONATED SAMPLE–IR/LRMS; TCO/GRAV.
1. TCO/GRAV. 2. TOTAL SAMPLE–IR 3. LC FRACTIONATED SAMPLE–IR/LRMS; TCO/GRAV.
1. GRAV. 2. TOTAL SAMPLE –IR 3. LC FRACTIONATED SAMPLE –IR/LRMS; GRAV.
1. TCO/GRAV. 2. TOTAL SAMPLE –IR 3. LC FRACTIONATED SAMPLE –IR/LRMS; TCO/GRAV.
1. GRAV. 2. TOTAL SAMPLE –IR 3. LC FRACTIONATED SAMPLE –IR/LRMS; GRAV.

*ANALYSIS ENDS HERE IF RESIDUE < 10 PERCENT OF TOTAL PARTICULATE CATCH.

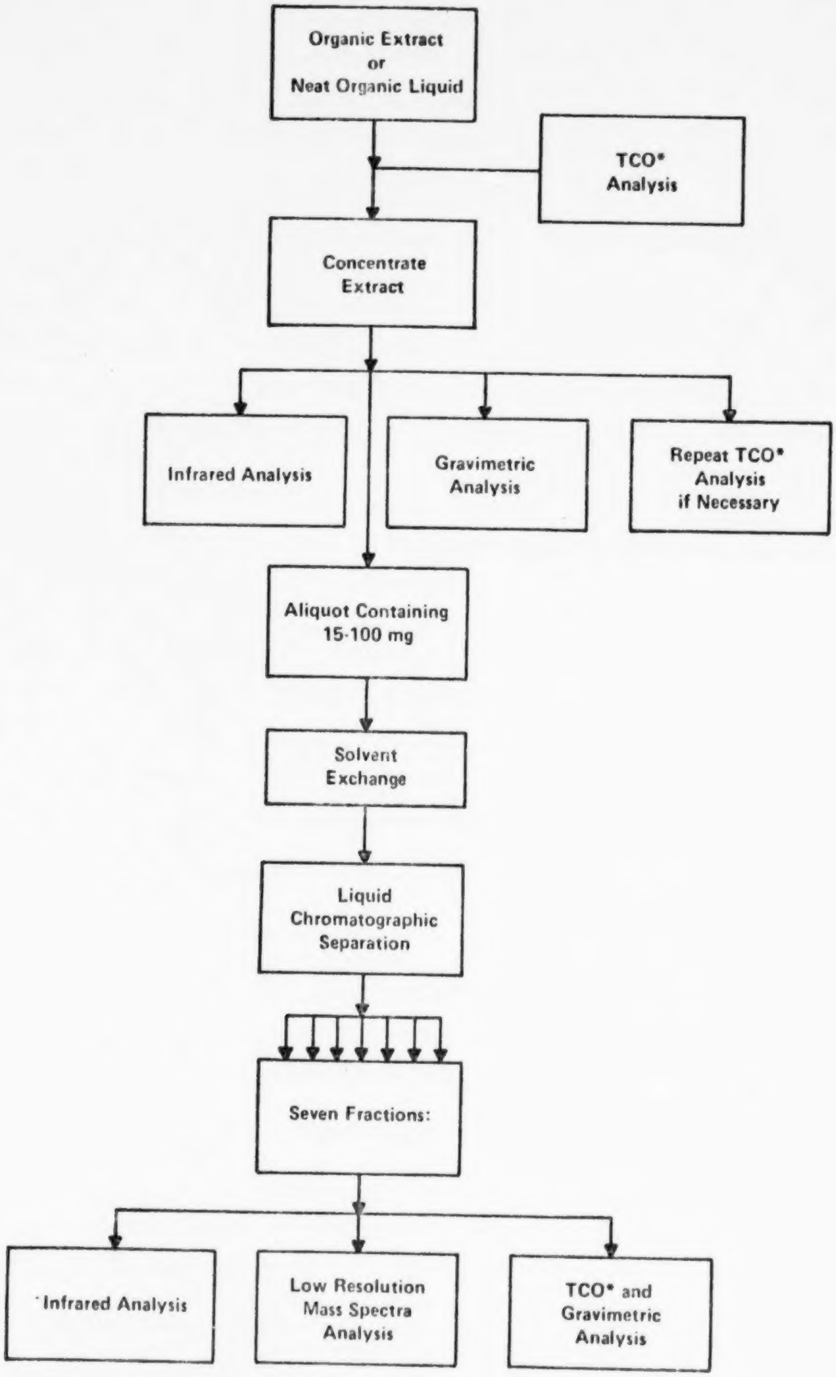
Figure 29. Multimedia organic analysis overview.

TABLE 15. SUMMARY OF EXPECTED DATA FROM LEVEL 1 ORGANIC ANALYSIS

Sample	Onsite GC	Weigh	Extract	TCO	GRAV	IR	LC*
Gases--grab sample	√						
SASS							
>10 µm particulate		√	√		√	√	√
3-10 µm particulate		√					
1-3 µm particulate		√	√		√	√	√
<1 µm particulate		√					
Rinse of particulate modules and probe		√	√†		√†	√†	√†
XAD-2 resin combined with rinse of sorbent module			√	√	√	√	√
Sorbent module condensate			√	√	√	√	√
SOLIDS							
Flyash; clinker		√	√		√	√	√
Organic feed stock		√	√	√	√	√	√
Coal		√	√	√	√	√	√
LIQUIDS							
Effluent water			√	√	√	√	√
Organic feed stock				√	√	√	
Fuels				√	√	√	

*Includes GRAV + IR and TCO on all fractions; perform LRMS when criteria are exceeded.

†Do analysis if gravimetric results are greater than 10 percent of the total particulate catch.



*See section 9.4.1.

Figure 30. Organic analysis methodology.

As indicated in Figure 29, the extent of the sample preparation required varies with sample type. The low molecular weight, volatile species (boiling point <100° C) are determined by gas chromatography onsite and require no preparation. Organic liquids, such as fuel oils, will not need pretreatment and are placed directly into the analysis scheme. However, the majority of the samples, including the SASS train components, aqueous solutions such as scrubber waters, and bulk solids such as coal or slag, require extraction with solvent prior to analysis. This extraction separates the organic portion of the samples from the inorganic species. The analysis of organic extracts or organic liquids then proceeds to initial quantitative analyses of volatile (TCO) and nonvolatile (GRAV) organic material and a preliminary infrared (IR) spectral analysis. The IR spectrum provides an indication of the types of functional groups present in the sample and a control checkpoint for subsequent analyses. All functional groups identified in this total sample should be accounted for in the succeeding steps.

The sample extract or organic liquid is separated by silica gel liquid chromatography (LC) using a 7-fraction solvent series of varying polarity. TCO and gravimetric analyses of each fraction are done to determine the distribution of the sample by the various class types. An IR spectrum is then obtained on each LC fraction for determination of the types of functional groups present. Low resolution mass spectra (LRMS) are also obtained on all fractions that exceed the concentration threshold in order to determine the principal compound types present in each fraction. For the sample streams identified in the Level 1 scheme, these threshold concentrations are:

a. Gas streams sampled with the SASS system--0.5 mg/m^3 computed at the source;

b. Aqueous slurry or solid samples--dependent on extract concentration;

c. Organic liquids--1 mg/LC fraction.

The decision is based on the sum of the TCO and GRAV analyses (Section 9.4) for each fraction.

It should be emphasized that sample contamination and solvent impurities are common problems in organic analysis. The best possible laboratory procedures must be used along with verified pure solvents. Blanks and controls are to be run for each stage in the analysis scheme, as specified in Chapter 2.

9.3 PREPARATION OF SAMPLE EXTRACTS

This section presents sample preparation procedures that are appropriate for most samples. The specific solvent indicated for the extraction is methylene chloride, which was selected because of its good solvent properties and high volatility (to facilitate concentration). This solvent should be used except in cases with unusual requirements, for which an alternative procedure can be suggested and used after approval by the project officer and by the Process Measurements Branch, IERL-RTP.

Procedures for concentration and analysis of extracts are presented in Section 9.4.

9.3.1 Aqueous Solutions

Extraction of aqueous solutions should be carried out with methylene chloride using a standard separatory funnel fitted with a Teflon stopcock. The pH of the aqueous phase should be adjusted first to 2.0 ±0.5 with hydrochloric acid and subsequently to 12.0 ±0.5 with sodium hydroxide, using multirange pH paper for indication. Two extractions are to be done at each pH, using a 250-mL volume of methylene chloride for each of the four extractions of a 10-L sample. The extractions may be performed in several batches on convenient-sized sample portions with corresponding amounts of solvent, but the entire 10-L sample must be extracted.

For the SASS train sorbent module condensate, the volume of aqueous solution should be measured and the quantity of methylene chloride adjusted proportionately.

To avoid the necessity of shipping large quantities of water, the extractions should preferably be done onsite whenever facilities will permit contamination-free conditions. If formation of emulsions is encountered, the samples may be shipped to the laboratory for extraction. Centrifugation at about 2,000 rpm has been found to be an effective way to break the emulsion in several studies.

9.3.2 Solids, Particulate Matter, and Ash

All solid material including waste products, raw materials, cyclone, probe and filter particulate, and ash are extracted for 24 h with methylene chloride in a Soxhlet apparatus. When sample quantities are limited, such as in the case of SASS cyclone catches, the designated solid sample aliquots, remaining after a small portion has been set aside for inorganic and particle morphology analysis, should be taken for the extraction. (See Table 11, Chapter 4.) When kilogram quantities of the sample material are available, optimal sample sizes should be used for these determinations. Bulk lumpy solids, such as coal, should be crushed to a size that will pass a 60-mesh screen before extraction, using a procedure such as that in ASTM D 2013, "Preparing Coal Samples for Analysis" (ref. 74). The sample is held in the thimble with a plug of glass wool and a stainless steel screen during the extraction to avoid carryover of the sample.

9.3.3 Slurries and Sludges

The sludge/slurry sample category can span a tremendous range, including slurries and solid or semisolid sludges containing up to 95 percent water. Some of these materials are very difficult to handle and no one procedure will work for all of them. The basic Level 1 approach is to determine whether the sample is best treated as a solid, a liquid, or by a combination of procedures. The protocol will involve, in most cases, tests on small portions of the 1-kg sample to determine the best procedure prior to committing the entire sample. The stepwise protocol follows.

> If the physical character of the sample permits, treat it as a solid by transferring the whole sample to a Soxhlet thimble and extracting for 24 h with methylene chloride. Do not dry sample before extracting. Determine wet weight of sample taken by weighing sample container before and after transferring sample to thimble. If an aqueous phase is noticed in the organic extract, this should be separated and removed prior to concentration.
>
> If the sample state does not appear compatible with direct Soxhlet extraction (i.e., wet sludge/slurry of high liquid content), select a treatment procedure as follows:
>
> 1. Take a 10-mL portion of the sample (shaking vigorously first, if necessary, to facilitate a fairly representa-

tive sampling) and place in a 15-mL centrifuge tube. Add 2 mL methylene chloride. Shake well and allow to settle for at least 30 min. Then:

a. If sample dissolves completely, treat the sample like a neat organic liquid--no sample preparation is required.

b. If a clean two-phase (organic-aqueous) separation is achieved, treat the sample like an aqueous sample.

c. If a clean two-phase separation is not achieved (i.e., if an emulsion forms, or if the apparent solvent recovery is low, or if a three-phase system with solids suspended in organic layer or between organic and aqueous layers is present), centrifuge the mixture. If a clean two-phase system then results, treat sample as in 1.b. above. If not, test sample as suggested in 2., below.

2. Take a 10-mL portion of the sample (shaking vigorously first, if necessary, to facilitate a fairly representative sampling) and place in a 15-mL centrifuge tube. Centrifuge. If phases separate, treat the solid phase by Soxhlet extraction. The liquid phase is treated like an aqueous sample or, if organic, like a neat organic liquid. The several extracts generated for this type of sample should be recombined--taking the same fraction of each--prior to organic analysis.

Occasionally a sludge/slurry sample may be encountered for which none of the above methods will be satisfactory. In those instances, the EPA project officer and appropriate PMB personnel should be consulted for guidance.

9.3.4 SASS Train Rinses

For each SASS train run there are two samples of this type, one from the rinse of the particulate portions (cyclones and filters), and a second from the rinse of the sorbent module. The solvent mixture used for the particulate rinses is 1:1 (v:v) methylene chloride:methanol. This rinse should be dried and weighed. If the residue quantity is greater than 10 percent of total filter and cyclone catch, the full complement of analytical tests should be performed. (See Figure 29.) The rinse for the gas conditioner and sorbent module is methylene chloride alone. It should be added to the Soxhlet solvent reservoir prior to XAD-2 extraction. This will result in a combined rinse and extract characterization for organic compounds. (See Figure 29.)

9.3.5 Sorbent Trap

The XAD-2 resin from the sorbent trap is removed from the SASS train cartridge and homogenized, and a 5-g portion is removed for the inorganic analysis. The balance of the resin is extracted with methylene chloride to remove the organic material. A large Soxhlet extraction apparatus, available from several manufacturers*, must be used to extract the 400 mL of resin. The resin is transferred to a previously cleaned glass extraction thimble†. A glass wool plug and stainless steel screen are used to secure the resin, which would otherwise float on the methylene chloride. Approximately 1 L of methylene chloride is added to the 2-L reflux flask. (The dumping volume of an appropriate commercial extractor is 750 mL.) A larger Soxhlet extractor may be used if available and an appropriate increase in the reflux solvent volume made. The boiling solvent in the flask should be examined periodically because additional methylene chloride may be needed to replace that lost by wetting the resin and by volatilization. The resin is extracted for 24 h. If water is extracted from the XAD-2 resin during this procedure, as evidenced by two phases in the liquid portion, segregate them with a separatory funnel before concentrating the methylene chloride. The aqueous fraction from this separation is added to the condensate catch before it is extracted at the two pH levels.

9.4 ANALYSIS OF SAMPLES FOR ORGANICS

The analysis of each of the prepared or isolated samples for organic compounds follows the scheme introduced in Figure 30. The overall scheme is based upon an initially recommended scheme (ref. 95), which has been revised with information from subsequent laboratory evaluations (ref. 96).

Qualitative analyses of organic compounds are accomplished by the LC/IR/LRMS procedure, which will provide reliable data on the compound types present in the sample or organic extract. However, compounds with boiling points below about 100° C will not be captured in the SASS train or retained in the organic extracts. Consequently, a separate field gas chromatography procedure has been included for the analysis of this range of materials (see Chapter 3), which gives a limited amount of qualitative information (retention times) as well as quantitative information.

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*For example, Ace Glass Incorporated (catalog No. 6810-10) or Lab Glass (catalog No. LG-6910-100).

†Thimbles of borosilicate glass with fritted glass discs must be specially fabricated for this size Soxhlet extractor. Do not use cellulose thimbles.

Quantitative analysis of moderately volatile materials (bp 100° C to 300° C) is achieved by a gas chromatographic procedure applied to various organic solvent extracts, organic liquids, and SASS sorbent module rinses. This Total Chromatographable Organics (TCO, Section 9.4.1) analysis is not appropriate for extracts from samples that do not contain low boiling organics, such as SASS particulate material collected at 200° C. Quantitative analysis of nonvolatile organic sample components (bp >ca. 300° C) in all extracts is achieved by evaporating an aliquot of extract to dryness and weighing the residue (GRAV procedure).

In summary, TCO analyses of extracts and organic liquids are performed prior to any concentration step. It is then necessary to obtain an IR on a portion of this material, to do a gravimetric analysis on an aliquot, and to concentrate the extract for the LC separation. The appropriate stage to conduct each of these steps (gravimetric analysis, IR, concentrate) will depend on the quantity and solubility of the sample as described in the following sections. For many samples, quantitative analyses (TCO and/or GRAV) may be required both before and after concentration.

9.4.1 Total Chromatographable Organics (TCO) Analysis

As previously stated, the TCO analysis is necessary for quantification of materials with boiling points in the range of 100° to 300° C. This analysis is applied to all samples that might contain compounds in this volatility range. These include organic liquids, many solid sample extracts, aqueous sample extracts, extracts from the SASS train sorbent module samples, and LC fractions obtained for those samples. However, particulate samples collected at the specified 205° C SASS train oven temperature or residues from high temperature processes do not require TCO analysis. If, for some special circumstance, the front half of the sampling train is run at a temperature lower than 200° C, then both the TCO and the gravimetric procedures should be applied to the extracts of cyclone particulate catch.

Because materials in the TCO volatility range may be lost to varying degrees during solvent evaporation, it is important that this analysis be performed on extracts and solutions prior to any concentration step. It will also frequently be desirable to repeat the TCO analysis later on the concentrated extract. When the original analysis shows a low TCO value, corresponding to a concentration of less than about 40 mg/L in the extract, the TCO analysis should be repeated on a concentrated extract. This will give a more reliable estimate than that obtained by multiplying the original low concentration estimate by the large volume of unconcentrated extract.

For determination of TCO, a 1- to 5-μL portion of the extract is analyzed by GC using a flame ionization detector. A 1.8 m x 3 mm O.D. (6 ft x 1/8 in.) column of 10 percent OV-101 on 100/120 mesh Supelcoport has been used successfully for this analysis. Other silicone phases (OV-1, etc.) may work as well, but a 10 percent loading is recommended. The GC is operated isothermally at about 30° C--or room temperature--for 6 min after sample injection and then programmed at approximately 20° C/min to 250° C and held at 250° C as long as necessary for complete elution of sample. Injector temperature of 275° C and detector temperature of 300° C are appropriate. Slight modifications in the temperature and duration of the initial hold period may be necessary to accommodate variations in individual GC systems.

Quantitative calibration of the TCO procedure is accomplished by use of mixtures of known concentrations of the normal hydrocarbons C_8, C_{12}, and C_{16}. The quantitative calibration standards should be prepared to cover the concentration range to be studied. Retention time limits corresponding to the TCO range of boiling points are defined by the peak maxima for n-heptane (C_7, bp 98° C) and n-heptadecane (C_{17}, bp 303° C). Therefore, integration of detector response should begin at the retention time of C_7 and terminate at the retention time of C_{17}. By this procedure, the integrated area will cover material in the boiling range of 100° C to 300° C. (The C_7 and C_{17} peaks should not be included in the quantitative calibration.)

In the TCO analyses, it is important that the observed values of total integrated area for samples be corrected by subtracting an appropriate solvent blank prepared (i.e., concentrated) in the same manner as the samples. The blank should be checked on each of the seven LC solvent mixtures.

The results of each TCO analysis should be reported as one number, in milligrams, corresponding to the total quantity of material in the 100° to 300° C boiling range in the original sample collected (see Figure 31). The TCO data are thus analogous to the results obtained by gravimetric analysis. The chromatograms themselves contain some additional data beyond the TCO values (i.e., retention times and areas of individual peaks) and should be retained until the Level 1 sampling and analysis effort has been completed.

9.4.2 Gravimetric (GRAV) Analysis

The gravimetric analysis is used for quantification of organic sample components with boiling points higher than 300° C. This analysis should be done after the sample extract has been concentrated, since it is recommended to weigh at least 10 mg of sample in a gravimetric analysis, when possible. Weighing to a precision of ±0.1 mg is adequate for purposes of Level 1 analysis. Sample and tare weights should be obtained by drying to "constant weight" (±0.1 mg) in a desiccator over silica gel or Drierite. In performing a gravimetric analysis on a large volume sample (i.e., >50 mL), no more than 5 mL of extract should be evaporated to dryness. For extracts concentrated to 10 mL, a 1-mL aliquot is taken for GRAV analysis. The GRAV results should be reported as one number for the entire sample (see Figure 31). The infrared analyses called for in Level 1 organic analysis can be performed on the residues from the GRAV procedure, provided that the weighing dishes were successively rinsed with distilled water, methanol, and methylene chloride before use.

9.4.3 Concentration of Extracts and Solvent Exchange Procedure

After the initial TCO* analysis, it will usually be necessary to concentrate the organic extracts to a volume of 10 mL for subsequent analysis. It is recommended that concentration to slightly less than 10 mL volume (i.e., 8 or 9 mL) be accomplished using a Kuderna-Danish apparatus with a 3-ball Snyder column for volumes less than 1 L, and a rotary evaporator for volumes that initially exceed 1 L. It is essential that the extract not be reduced to dryness at this point in the scheme to prevent loss of TCO range material. The concentrated extract should then be transferred to a convenient graduated container (e.g., Kuderna-Danish receiver or centrifuge tube) and the volume restored to 10 mL. The concentration process should be stopped if material begins to drop out of solution. In that case, the extract should be restored to a convenient volume in which the material is redissolved. The original TCO* analysis may provide guidance as to the degree of concentration that is required for each particular sample. The objective is to achieve a final concentration of not more than 100 mg/mL and a final volume of not less than 10 mL.

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*On all samples except SASS particulate fractions and residues from high temperature processes.

At this stage in the analysis sequence, a GRAV determination is done and the TCO* determination is repeated.† A 1-mL aliquot is used for the GRAV analysis and a 5-μL aliquot is used for the TCO. If the sum of TCO plus GRAV is <15 mg for the total sample, the LC separation is not performed and the Level 1 analysis is concluded by obtaining IR and LRMS spectra on the sample. If the sum of TCO plus GRAV is ≥15 mg, the LC separation is performed. An IR spectrum is also obtained on the residue from the GRAV analysis or on a separate aliquot of extract. A portion of the concentrated extract that contains about 100 mg of organic material, if possible, is taken for the LC. Smaller quantities down to a lower limit of 15 mg may be used if necessary.

The LC separation procedure requires that both methylene chloride solvent and water be eliminated before the sample extract is applied to the silica gel column. Otherwise, the required aliphatic/aromatic and subsequent compound class separations will not be achieved. Extracts that do not contain low boiling organics, such as SASS train particulate materials or other materials collected at temperatures exceeding 200° C (400° F), can be evaporated to dryness with silica gel, as detailed below, before LC analysis.

---

*On all samples except SASS particulate fractions and residues from high temperature processes.

†Unless the initial TCO values for the unconcentrated extract exceeded the guideline of 40 mg/L (TCO).

Extracts containing appreciable quantities of TCO material (>2 mg) must be transferred to the LC columns without being evaporated to dryness. For these samples, a solvent exchange procedure is required to minimize losses of volatile sample components. An aliquot of the methylene chloride solution containing 15 mg (minimum) to 100 mg (preferred) of sample is taken for solvent exchange into cyclopentane; the detailed procedure is given below. Normal hydrocarbon solvents are not to be substituted for the cyclopentane; pentane boils too low (36° C, below methylene chloride) and hexane boils too high (68° C) for the solvent exchange. The solvent exchange and removal of water from the sample extracts is accomplished as described in Section 9.4.4.3.

9.4.4 Liquid Chromatographic (LC) Separation

All sample extracts, neat organic liquids, and SASS-train-dried probe/cyclone rinse extracts are subjected to LC separation if sample quantity is adequate. An aliquot of the concentrated extract containing 100 mg of organic matter is preferred for the LC, but smaller quantities down to a lower limit of about 15 mg may be used. The sample components are separated according to polarity on silica gel using a step gradient elution technique. The detailed procedure for the LC separation is given below:

Column: 200 mm x 10.5 mm ID, glass with Teflon stopcock, water-jacketed with inlet water temperature in the range of 18° to 22° C and sufficient flow to maintain this temperature through to the outlet.

Adsorbent: Davison, Silica Gel, 60-200 mesh, Grade 950 (available from Fisher Scientific Company) is to be used; no other types or grades of silica gel can be substituted. This material should be cleaned prior to use by sequential Soxhlet extractions with methanol, methylene chloride, and pentane. This adsorbent is then activated at 110° C for at least 2 h just prior to use, and cooled in a desiccator.

Drying Agent:	Sodium Sulfate (Anhydrous, Reagent Grade). Clean by sequential Soxhlet extraction for 24 h each with methanol, methylene chloride, and pentane. Dry for at least 2 h at 110° C just prior to use and cool in a desiccator.

9.4.4.1 Procedure for Column Preparation--

The chromatographic column, plugged at one end with a small portion of glass wool, should be slurry packed with 6.0 g of freshly activated silica gel in n-pentane. A portion of properly activated silica gel weighing 6.0 ±0.2 g occupies 9 mL in a 10-mL graduated cylinder. The total height of the silica bed in this packed column is 10 cm. The solvent void volume of the column is 2 to 4 mL. When the column is fully prepared, allow the pentane level in the column to drop to the top of the silica bed so that the sample can be loaded for subsequent chromatographic elution.

After packing the silica gel column, add 3 g ±0.2 g clean sodium sulfate to the top of the column. Vibrate for 1 min to compact. The sodium sulfate should occupy 2 mL in a 10-mL graduated cylinder. The sodium sulfate will remove small quantities of water from the organic extract; however, appreciable quantities of water will solidify the sodium sulfate, inhibiting proper flow through the column. Therefore, it is advisable that if enough water is present in the sample to form two layers, it should be removed by another method--pipette or separatory funnel.

9.4.4.2 Evaporation of Sample Extracts with Low TCO ($\leq$2 mg original sample)--

For these samples, the aliquot of extract containing 15 mg (minimum) to 100 mg (preferred) of material is added to a small amount of silica gel, the solvent is allowed to evaporate, and the residue plus silica gel is transferred to the LC column with the aid of a microspatula. The container is rinsed as described in Section 9.4.4.5.

9.4.4.3 Solvent Exchange of Sample Extract with High TCO (>2 mg original sample)--

An aliquot of methylene chloride extract containing 15 mg (minimum) to 100 mg (preferred) of material is added to 200 mg of silica gel in a graduated receiver. The volume of extract is carefully reduced to 1 mL at ambient temperature under a gentle stream of nitrogen (tapped from a liquid nitrogen cylinder, if possible, to minimize impurities). The solvent evaporates rapidly so it is important that this operation be done under constant surveillance to insure that the volume is not reduced below 1 mL. It is also necessary to warm the samples slightly, either by hand or water bath, at ≤40° C, to prevent condensation of atmospheric moisture in the sample due to evaporative cooling. One milliliter of cyclopentane is added and mixed by gentle agitation. The volume is reduced to a total of 1 mL as before. A second milliliter of cyclopentane is added, mixed, and the volume is again reduced to 1 mL. The exchange is repeated with a third milliliter of cyclopentane. After the volume has been reduced to 1 mL for this last time, the solvent mixture will be ≤5 percent methylene chloride. This is sufficiently low to prevent breakthrough of aromatic sample components into the aliphatic hydrocarbon fraction, LC1.

The cyclopentane and silica gel are transferred to the top of the previously prepared LC column using a Pasteur pipette. The container is rinsed as described in Section 9.4.4.5.

9.4.4.4 Neat Organic Liquids--

A 100-mg sample is weighed into a tared glass weighing funnel and mixed with about 200 mg of silica gel using a microspatula. The sample is then transferred to the top of the column. The container is rinsed as described in Section 9.4.4.5.

When neat organic liquids are fractionated by the liquid chromatography scheme, they have the same theoretical gravimetric detection limitations as other samples separated by this means, 0.1 mg/100 mg or 0.1 percent of the sample applied. Since these aliquots are neat samples and do not have concentration factors as multipliers, the resultant detection limits for minor components are 1 g/kg at best.

9.4.4.5 Chromatographic Separation into Seven Fractions--

Table 16 shows the sequence for the chromatographic elution. In order to insure adequate resolution and reproducibility, the column elution rate is maintained at 1 mL/min.

TABLE 16. LIQUID CHROMATOGRAPHY ELUTION SEQUENCE

Fraction	Solvent composition	Volume (mL)
1	Pentane	25
2	20% Methylene chloride in pentane	10
3	50% Methylene chloride in pentane	10
4	Methylene chloride	10
5	5% Methanol in methylene chloride	10
6	20% Methanol in methylene chloride	10
7	50% Methanol in methylene chloride	10

The volume of solvents shown in Table 16 represents the solvent volume added to the column for that fraction. If the volume of solvent collected is less than the volume actually added due to evaporation, restore the fraction volume to the proper level with fresh solvent. In all cases, the solvent level in the column should be at the top of the gel bed, i.e., the sample-containing zone, at the end of the collection of any sample fraction. The fractions are retained as solutions for TCO analyses.

After the first fraction is collected, rinse the original sample container or weighing funnel with a few milliliters of Fraction 2 solvent (20 percent methylene chloride/pentane) and carefully transfer this rinsing into the column. Repeat with each successive solvent mixture in turn.

Add each new solvent to the column slowly to minimize disturbing the gel bed and eliminate the trapped air bubbles, particularly in the zone of the sample-containing silica gel.

After each sample is collected, an aliquot (1 to 5 µL) is taken for TCO analysis of each fraction (unless the sample taken for LC had a TCO of ≤ 2 mg). Also, an aliquot (10 ml for Fraction 1 and 5 mL for Fractions 2-7) is transferred to a tared aluminum micro weighing dish for evaporation and gravimetric analysis. The GRAV data for Fraction 7 must be corrected for a blank contributed by a small quantity of silica gel that dissolves in the highly polar eluent. The blank value is determined by running an LC column to which no sample is added; it is on the order of 0.9 ±0.1 mg in LC7 (10 mL).

After TCO and GRAV determinations, the fractions are analyzed by IR and, when the quantity is sufficient, by LRMS (see Section 9.4.6).

The objective of the LC procedure is to separate the sample into fractions of varying chemical class type to facilitate subsequent analyses. The LC separation procedure is not a high resolution technique and, consequently, there is overlap in class type between many of the fractions. Figure 31 shows a sample LC report with a number of compound classes represented in the eluent.

The results of the LC fractionation procedure include quantitative estimates of TCO and GRAV range materials in each of seven fractions. In most cases, the quantity of material actually taken for the LC separation is only a portion of the total sample, and the amount taken should be stated in the report. The actual, measured TCO and GRAV values for the LC fractions should be multiplied by the appropriate factor (total sample quantity ÷ quantity taken for LC) to give the corresponding total sample values. It is then useful to convert these quantitative estimates into equivalent concentrations at the source in order to facilitate comparisons with various decision criteria. Figure 31 illustrates the format for reporting LC fractionation data, with an example from a SASS train sorbent trap extract. Note that GRAV analyses involve weighing to the nearest 0.1 mg. TCO values are reported to the nearest 0.1 mg, also.

9.4.5 Infrared Analysis

The total sample extract, or neat liquid, and the 7 LC fractions are analyzed by infrared (IR) spectrophotometry. A grating spectrophotometer should be used and the following instrument conditions adhered to.

1. Resolution: For dispersively measured spectra, the spectral slit width should not exceed 4 cm^{-1} through at least 80 percent of the wave number range.
2. Wave number accuracy: ±4 cm^{-1} below 2,000 cm^{-1} and ±15 cm^{-1} above 2,000 cm^{-1}.
3. Noise level: No more than 2 percent peak to peak.
4. Baseline flatness: The I_0 or 100 percent line must be flat to within 5 percent across the recorded spectrum.

LC REPORT

SAMPLE: II-3 SORBENT TRAP EXTRACT

	TCO mg	GRAV mg	TCO + GRAV Total mg	Concentration mg/ (m^3, L, or kg)
Total Sample[1]	106	386	492	82
Taken for LC[2]	23	84	107	18
Recovered[3]	17	74	91	15

Fraction	TCO in mg				GRAV in mg				TCO + GRAV Total mg	Concentration mg/ (m^3,L, or kg)
	Found in Fraction	Blank	Cor-rected	Total[4]	Found in Fraction	Blank	Cor-rected	Total[4]		
1	0.3	0.0	0.3	1.4	2.5	0.0	2.5	11.5	12.9	1.9
2	3.3	0.1	3.2	15.0	1.0	0.1	0.9	4.1	19.1	3.2
3	12.0	0.5	11.5	54.0	56.4	2.5	53.9	247.9	301.9	50.0
4	0.1	0.0	0.1	0.5	2.2	0.1	2.1	9.7	10.2	1.7
5	0.2	0.1	0.1	0.5	6.8	0.5	6.3	29.0	29.5	4.9
6	0.7	0.0	0.7	3.2	3.6	0.2	3.4	15.6	18.8	3.1
7	0.1	0.0	0.1	0.5	0.6	0.0	0.6	2.8	3.3	0.6
Sum	16.7	0.7	16.0	75.1	73.1	3.4	69.7	320.6	395.8	65.9

1. Quantity in entire sample, determined before LC
2. Portion of whole sample used for LC, actual mg
3. Quantity recovered from LC column, actual mg
4. Total mg computed back to total sample

Figure 31. Sample LC report.

5. Energy: The instrument should be purged with dry gas or evacuated so that atmosphere water bands do not exceed the allowable noise level (2 percent) when the instrument is ued in a double beam mode.
6. Spectral range: Spectra should be recorded, without gaps, over the spectral range 3,800-600 cm^{-1}.
7. False radiation: Not to exceed 2 percent.

IR spectra are obtained in absorbance units on samples held between two NaCl salt plates using methylene chloride to transfer the sample to the plates. KBr pellets can also be used if films (from $MeCl_2$) will not give satisfactory spectra, i.e., material is a crystalline solid. Sample quantity and instrument parameters are adjusted so that the maximum signal of the strongest peak is less than 1.0 absorbance.

Spectra are interpreted in terms of functional group types present in the sample or LC fraction. The many reference texts (refs. 96-101) in this area are of considerable help in interpreting the IR spectra. The interpretation of the spectra should also be guided by consideration of the LC fractionation scheme and the LRMS results (when available).

The results of the IR analysis should be reported in the format shown in Figure 32 according to the following guidelines:

a. The frequency reported should be the peak maximum, or a range may be reported instead for broad peaks with no well-defined maximum.
b. Absorbance values should be measured by baseline technique. The intensity is reported relative to the strongest peak in the spectrum on a percentage absorbance basis.

S = strong, 70-100 percent of the absorbance value of the strongest peak.

M = medium, 30-70 percent of the absorbance value of the strongest peak.

W = weak, 0-30 percent of the absorbance value of the strongest peak.

When a peak is of borderline intensity, it should be labeled "m." Finer intensity ratings such as M-S or W-M are not appropriate.

IR REPORT

SAMPLE: II-3-LC6

Wave Number (cm^{-1})	Intensity	Assignment	Comments
3400	M	OH, NH	Broad
3050	W	unsat'd CH	
2850, 2920	M	sat'd CH	
1710	S	acid, ketones	
1680	M	amide, ketones	
1600	M	aromatic C = C	
1450	M	CH_2	
1060	S	Si–O, ether	Broad
740	M	subst. pyridine, C–Cl	

Figure 32. Sample IR report.

c. The assignment/comments column indicates the functional group(s) to which the peak is attributed*. This column may also contain single-word descriptors of peak shape such as "broad," "doublet," "shoulder."

d. All weak, medium, and strong peaks must be reported.

e. A copy of the infrared spectrum should be retained at the laboratory for 3 years should further reference to it be needed.

As a matter of quality control, the IR bands observed with each LC fraction should be compared to those observed with the total sample. Additional bands in any of the fractions would indicate the introduction of impurities or decomposition on the column. The IR bands observed with the total sample but not with any of the LC fractions would indicate loss of material onto the column.

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*All features of the IR spectrum, such as presence or absence of bands at other related IR frequencies, should be considered in making the functional group assignments.

9.4.6 Low Resolution Mass Spectrometry (refs. 102-105)

A low resolution mass spectrum (LRMS) is obtained on each LC fraction that has sufficient quantity (TCO plus GRAV), when referenced back to the source, to exceed decision criteria concentrations. The Process Measurements Branch guidelines recommended for general Level 1 purposes are:

Gas--SASS train samples	0.5 mg/m^3
Ambient air--particulate	1 μg/m^3
Solids	1 mg/kg
Aqueous solutions	0.1 mg/L

An LRMS analysis is to be done on any LC fraction that corresponds to a source concentration higher than these levels.

In the event that other, more stringent criteria are determined to be appropriate for a particular environmental assessment, then the cutoff point for performing LRMS will change accordingly. For example, if MEG/MATE (Multimedia Environmental Goals/Minimum Acute Toxicity Effluent) concentration values are to be used in making Level 1 decisions, then LRMS must be done on all LC fractions for a SASS sample. This is because MATE values are sufficiently low that in each LC fraction there is at least one compound category that might be present whose level of concern would be exceeded by any detectable quantity of material.

In order to minimize the cost of the Level 1 organic analysis, it is desirable to keep the total number of LRMS analyses required as low as possible. An LRMS analysis must always be run on any LC fraction that exceeds the Level 1 concentration criteria given above. However, if the more stringent (MEG/MATE) cutoff criteria are used, it is acceptable, for LRMS purposes only, to combine fractions falling below the Level 1 concentration criteria, according to the following scheme:

LC1 = LRMS-1
LC2 plus LC3 = LRMS-2, 3
LC4 plus LC5 = LRMS-4, 5
LC6 plus LC7 = LRMS-6, 7

This will allow LRMS results to be obtained on all LC fractions in a minimum number of separate LRMS analyses. The IR data obtained with each LC fraction should be considered before making the decision to combine fractions. If the IR spectra of two fractions considered for combination are vastly different, those fractions should probably not be combined as the LRMS of the mixture will be especially difficult to interpret.

The mass spectrometer used in this determination should have a resolution ($\bar{M}/\Delta M$) of 800 to 1,000, batch and direct probe inlet, variable ionizing voltage source, and electron multiplier detection. Samples with significant quantities of TCO range material (>2 mg) should be analyzed by insertion in the batch inlet. All samples that meet the decision criteria for quantity (TCO plus GRAV) will require analysis via the direct insertion probe. A small quantity of sample is placed in the probe capillary and inserted into a cool source. The temperature is then programmed up to vaporize the sample. Spectra are recorded periodically through this period. Spectra are normally obtained at 70 eV ionizing voltage, but low voltage (10 eV) spectra may provide much simpler data and thus aid in interpretation in some cases.

The mass spectroscopist should integrate the interpretation of the batch and probe mass spectra obtained on a particular sample to provide one report describing sample chemistry. Details of quantitation of LRMS data are too numerous to be addressed in this manual.

Interpretation of the mass spectra is guided by knowledge of the LC separation scheme, the IR spectra, and other information about the source. In reporting the results of the LRMS analysis, the basic philosophy is to present increasingly more specific data as the complexity (or simplicity) of the spectra will allow. The first level of reporting is to identify compound classes. If possible, or appropriate, one should then attempt to identify the subcategory compound classes present in the fraction. Finally, specific compounds should be identified, if possible to do so from the spectra. Where possible, the molecular weight range and composition of each category should be estimated with a rating of 100 = major, 10 = minor, and 1 = trace.

It should be possible, using this methodology, to account for nearly all observed species by selection from a relatively small list of compound categories and subcategories. A tentative list of such categories has been assembled in Table 17. The primary reference for selecting these categories was the MEG list, which seems to do an adequate job of representing all probable major compound classes. Some few categories were not in the MEG list and have been added here.

TABLE 17. CATEGORIES FOR REPORTING LRMS DATA

Category (Subcategory)	Most probable LC fraction*	Category (Subcategory)	Most probable LC fraction*
Aliphatic hydrocarbons	1	Phenols	6
(Alkanes)	1	(Alkyl, etc.)	6
(Alkenes)	1	(Halogenated phenols)	6
(Alkynes)	1	(Nitrophenols)	6
Halogenated aliphatics	1,2	Esters	6
(Saturated)	1,2	(Phthalates)	6
(Unsaturated)	1,2	Ketones	6
Aromatic hydrocarbons	2,3	Amines	6
(Benzenes)	2,3	(Primary, secondary, tertiary)	6
Halogenated aromatic hydrocarbons	2,3	(Hydrazines, azo compounds)	6
Nitro aromatic hydrocarbons	4,5	(Nitrosoamines)	6
Fused alternate, nonalternate hydrocarbons	2,3	Heterocyclic nitrogen compounds	
MW < 216 (methyl pyrene)	2,3	(Indoles, carbazoles)	4
MW > 216	2,3	(Quinolines, acridines)	6
Ethers	4	Alkyl sulfur compounds	6
(Halogenated ethers)	4	(Mercaptans)	6
Epoxides	4	(Sulfides, disulfides)	6
Aldehydes	4	Heterocyclic sulfur compounds	
Heterocyclic oxygen compounds	3,4	(Benzothiophenes)	4
Nitriles	4	Sulfonic acids, sulfoxides	7
(Aliphatic)	4	Amides	6
(Aromatic)	4		
Alcohols	6	Carboxylic acids	6,7
(Primary, secondary, tertiary)	6	Silicones	2,3,4
(Glycols)	6	Phosphates	5,6,7

*Possible assignments. Fractions 4-5, 5-6, 6-7 generally overlap to a considerable extent. Also, additional components of a particular molecule may cause it to elute in an LC fraction other than that expected. For example, a short-chain ester would probably elute in LC fraction 5 or 6 whereas a long-chain ester would elute in Fractions 3 or 4.

The list in Table 17 is also organized somewhat differently than the MEG list to be more compatible with the nature of the mass spectrometry data. It should be strongly emphasized that the list probably does not include all identifiable compound categories. If interpretation of the spectra yields the identification of a category not included in this table, the category should be reported. At the same time, EPA/PMB should be notified of the need to add that category to the list. It will be possible in most cases to identify the spectra in terms of the compound categories listed in Table 17, but one should avoid force fits if another category seems more appropriate.

Interpretation of the mass spectral data should take full advantage of all other information known about the sample source, i.e., LC fraction and IR spectra. Since the LC separation does a reasonable job of dividing compound classes, the categories listed in Table 17 have been listed in order of their possible elution from the LC column. Where possible, some indication has been made as to the LC fraction in which the category might elute. These fraction assignments are known to be correct in some cases and are only estimates in others. Sometimes the sample characteristics will have minor effects on the fraction elution behavior. Again, the LC fraction indications should only be taken as a guideline. Figure 33 gives a completed example of a reporting format for the LRMS data. Blank forms may be found in Appendix A.

It is once again emphasized that interpretation of the LRMS data is best done using all available information, such as what one knows about the chemistry of the source being sampled, what species generally elute in the LC fraction being examined, and functional group data derived from the IR spectra.

9.5 ORGANIC ANALYSIS SUMMARY TABLES

At the end of the Level 1 organic analysis procedure, there will be an LC report, seven IR reports, and up to seven LRMS reports for each organic extract or neat organic sample. This is an unwieldy body of data from which to make a decision. The first step in reducing these data to a workable form is to prepare a single table that summarizes the organic analysis

LRMS REPORT

SAMPLE: II-3-LC6

Major Categories

Intensity	Category	MW Range
100	Ketones	180-280
100	Heterocyclic Nitrogen Compounds	167-253
10	Esters	
10	Carboxylic Acids	
10	Phenols	

Sub-Categories, Specific Compounds

Intensity	Category	m/e	Composition
100	Acridine	179	$C_{13}H_9N$
100	Fluorenone	180	$C_{13}H_8O$
10	Phenol	94	C_6H_6O
10	Cresol	108	C_7H_8O
10	Benzoic Acid	122	$C_7H_6O_2$
10	Carbazole	167	$C_{12}H_9N$
10	Methylacridine	193	$C_{14}H_{11}N$
10	Methylfluorenone	194	$C_{14}H_{10}O$
10	Anthraquinoline	229	$C_{17}H_{11}N$
10	Benzanthrone	230	$C_{17}H_{10}O$
10	Dibenzofluorenone	280	$C_{21}H_{12}O$
10	Dibutylphthalate	278	$C_{16}H_{22}O_4$
10	Methylbenzanthrone	244	$C_{18}H_{12}O$

Other

Figure 33. Sample LRMS report.

results for each extract. Figure 34 illustrates the organization of this table and the following paragraphs describe the various entries.

Space is allotted in the table heading for a sample identification code. It is assumed that each laboratory will have devised its own coding system (see Chapter 2) for uniquely identifying the various samples. It may be desirable to include the date, the name of the analyst, or other similar information.

The body of the table includes one column for each of the LC fractions and one column for summing the data. The first set of data entries is the quantitative analysis, transcribed from the LC report. The calculated total organic loading corresponding to each fraction is entered in the first row. This value is used in estimating the abundance of the various organic compound classes. The next two rows contain the estimated TCO and GRAV values to indicate the distribution of total volatile (bp 100°-300° C) and nonvolatile (bp >300° C) organic materials. This information can be useful later in the selection of appropriate decision criteria (Level 1, MATE, etc.) values for comparison with the Level 1 results. The results of the compound category analysis (primarily from LRMS data) are summarized in the bottom columns.

For those LC fractions that contained sufficient quantity to have been analyzed by LRMS, the results of the LRMS analyses are summarized in the table as follows: The major categories present in LC fraction 1 are listed at the left-hand side of the table and the approximate intensity (100, 10, or 1) for each category is entered in the LC1 column. To convert the LRMS intensity index to a concentration estimate for each organic compound category, the individual intensity value is divided by the sum of all intensities for the LC fraction and then multiplied by the total organic loading (mg/m^3) estimated for the fraction. This procedure is then repeated for the other LC fractions. Examples are worked in Figure 35 for two LC fractions, LC2 and LC4, of the same XAD-2 extract.

The results presented in Figure 34 illustrate the considerable overlap in chemical class composition that can be expected between some fractions in the Level 1 LC scheme. As noted earlier, this is not a high resolution separation technique and the various compound categories cannot be uniquely

ORGANIC EXTRACT SUMMARY TABLE

Sample Sorbent Extract–II-3

	LC1	LC2	LC3	LC4	LC5	LC6	LC7	Σ
Total Organics, mg	18.2	22.3	253	29.7	11.0	46.3	15.1	390
TCO, mg	5.2	19.	73.	6.7	3.7	5.3	0.1	110
GRAV, mg	13.	3.3	180.	23.	7.3	41.	15.	280

Category	Assigned intensity–mg/___(m^3, L, or kg)*							
Sulfur	100–0.6							0.6
Aliphatic HC's	10–0.06							0.06
Aromatics–Benzenes		10–0.06						0.06
Fused Arom 216		100–0.6	100–4	100–0.5				5.
Fused Arom 216		10–0.06	100–4	100–0.5				5.
Heterocyclic S		10–0.06	10–0.4	10–0.05				0.5
Heterocyclic N				10–0.05	–0.1[†]	100–0.7	10–0.02	1.
					–0.1[†]	10–0.07	100–0.2	0.3
Carboxylic Acids					–0.1[†]	100–0.7	10–0.02	1.0
Phenols					–0.01[†]	10–0.07	10–0.02	0.1
Esters					–0.01[†]	10–0.07		0.08

*Concentration for gas samples = mg/m^3, for liquid samples = mg/L, for solid samples = mg/kg. Fill in actual m^3, L, or kg value.

[†] Estimated assuming same relative intensities as LC6, since IR spectra of LC5 and LC6 are very similar.

Figure 34. Organic extract summary table.

LC 2

Total organics = 0.57 mg/m^3

Aromatic HC's-benzenes	10
Fused Arom <216 MW	100
Fused Arom >216 MW	10
Heteroyclic S Compounds	10

LC 4

Total organics = 6.6 mg/m^3

Fused Arom <216 MW	100
Fused Arom >216 MW	100
Heterocyclic S Compounds	10
Heterocyclic O Compounds	10

Calculation of Concentration Estimates by Category

$\sum$ intensities = 130

Aromatic HC's - benzene: $\frac{10}{130} \times 0.57 = 0.04\ mg/m^3$

Fused Arom <216 MW: $\frac{100}{130} \times 0.57 = 0.4\ mg/m^3$

Fused Arom >216 MW: $\frac{10}{130} \times 0.57 = 0.04\ mg/m^3$

Heterocyclic S Cmpds: $\frac{10}{130} \times 0.57 = 0.04\ mg/m^3$

$\sum$ intensities = 220

Fused Arom <216 MW: $\frac{100}{220} \times 6.6 = 3\ mg/m^3$

Fused Arom >216 MW: $\frac{100}{220} \times 6.6 = 3\ mg/m^3$

Heterocyclic S Cmpds: $\frac{10}{220} \times 6.6 = 0.3\ mg/m^3$

Heterocyclic O Cmpds: $\frac{10}{220} \times 6.6 = 0.3\ mg/m^3$

Figure 35. Sample calculations of concentration estimates from LRMS data.

assigned to particular LC fractions. The data do show the expected trend, in that LC2 is relatively richer in light aromatics (benzene and fused species with MW <216) than is LC4. The fact that adjacent LC fractions can be expected to show gradual changes in chemistry can serve as a useful guide for the analyst in detecting contamination. Very abrupt changes in apparent composition or the appearance of a compound class in an entirely unexpected fraction (i.e., phthalates in LC2 or paraffins in LC6) should be regarded with suspicion.

The overlap between fractions can also be used in estimating the composition of those fractions that did not contain sufficient material to trigger an LRMS analysis. For any LC fraction that was not analyzed by LRMS, it is suggested that the IR spectrum be compared with the IR's of the adjacent fractions. If a close correlation is found between two IR spectra, then this, together with the known behavior of the LC scheme, suggests that the two LC fractions have similar, though not identical, qualitative composition. It is therefore suggested that the total organics in the non-LRMS LC fraction be distributed over the same classes and in the same proportion as was done for the adjacent LC fraction whose IR spectrum was the best match. The error introduced by this procedure into the overall description of sample chemistry will be small, since only fractions with small amounts of material are excluded from the LRMS.

Concentrations estimated by this procedure should be identified with an asterisk in the organic extract summary table and an explanatory footnote should be included.

For those LC fractions for which only IR data are available, the procedure for estimating concentrations by compound class is as follows:

1. List all categories from Table 17 that could be in that fraction.
2. Assign a weighting factor of 100 to each category that appears to be present in the sample based on the IR spectrum.
3. Assign a weighting factor of 10 to each category for which functional groups were not identified.

Then, in the absence of evidence to the contrary, assume that categories with an intensity of 100 may constitute up to 50 percent of the total sample and those with an intensity of 10 up to 10 percent. Clearly, this procedure may "account for" more than 100 percent of the total sample. However, this conservative method of estimation seems necessary because it is not always possible to determine from the IR spectrum of a mixture alone how the various functional groups are assembled into molecules or classes.

Table 18 illustrates this procedure for an LC5 sample, assuming only IR and LC data were available. Concentrations estimated on the basis of IR and LC data only should be footnoted with a dagger in the organic extract summary table and an explanatory footnote should be included.

Once concentrations have been estimated for all compound categories identified in the seven LC fractions for a particular organic extract, or neat organic liquid, these values are summed across each row of the table. (See Figure 34.) This procedure condenses the information obtained on the various LC fractions to provide an integrated description of the chemical composition. In the case of liquid and solid samples, the summation column represents the total concentration/compound category information for the stream sampled. For gaseous streams, the summary report for each component of the SASS train must be added to determine the stream composition, as was shown in Table 15.

9.6 QUALITY CONTROL IN LEVEL 1 ORGANIC ANALYSIS

This discussion has been written for the analytical chemist, who can be presumed to be familiar with generally accepted standards of good laboratory practice. It is worthwhile, however, to reemphasize the importance of some procedures, in addition to sample preparation and analysis per se, which have a very significant impact on the overall quality of the analytical results. Some of those procedures, in particular those related to preventing and/or recognizing sample contamination, are especially critical in a Level 1 environmental assessment.

To insure adequate data quality, it is essential that blanks (controls) be analyzed along with the samples, as discussed in Chapter 2. There is no reliable way to identify spurious results and/or sample contamination other than by finding the same contaminant in a control sample.

TABLE 18. ESTIMATION OF FRACTION COMPOSITION FROM IR AND LC DATA ONLY

Sample LC 5 IR Report Wave number cm^{-1}	I	Assignments/comments	Total Organics = 0.28 mg/m^3 Categories most probable in LC 5	Assigned weighting factor	Estimated possible concentration (mg/m^3)*
3,400	S	OH or NH (broad)	Heterocyclic N compounds	100	0.14
3,050	M	Aromatic CH	Heterocyclic S compounds	10	0.03
2,850-2,950	S	Aliphatic CH	Sulfides, disulfides	10	0.03
2,230	M	C≡N or C≡C, cyanates or isocyanates	Nitriles	100	0.14
			Ethers	100	0.14
1,700	S	Ketone, carboxylic acid, aldehydes	Aldehydes, ketones	100	0.14
1,600	S	Conj. C=C or aromatic C=N, N-NO$_2$, C-N=O, Carboxylate	Nitroaliphatics	100	0.14
			Alcohols	100	0.14
1,530	M	C=N, C-NO$_2$	Nitroaromatics	100	0.14
1,420-1,450	S	CH$_3$, NH$_4$+, CH$_2$, Si-phenyl carbonates	Amines	100	0.14
			Phenols	100	0.14
1,050-1,300	M	Alcohol C-O, phenol C-O, ether C-O, C-F, various P-O compounds, various Si-O or Si-C compounds	Esters	10	0.03
700-850	S	Subst. benzene rings, some olefinic C-H, C-Cl, CF-CF, some peroxides			

*Total organics = 0.28 mg/m^3.

Control sample, of course, means more than a simple reagent blank for the analysis itself. The control sample and its handling throughout the laboratory sequence should be identical to the real sample and its handling, except that the real sample has been exposed to a process stream in a sampling procedure. For instance, an unexposed XAD-2 cartridge must be dumped, homogenized, and a 5-g aliquot reserved for the Parr bomb ashing and trace element assays. The remainder must be Soxhlet extracted and the extract subjected to the entire organics analysis sequence.

The procedures for cleaning the XAD-2 resin prior to use are specified in Appendix B. The quality control checks described in the appendix should be applied to each batch of resin before it is used in a field study.

Each lot of organic solvent (i.e., each new batch number) must be checked for contamination. A volume of solvent equivalent to that used in sample extraction should be evaporated to dryness. The residue should be weighed and examined by IR. If any significant quantity of organic contamination is found, the solvent batch must be redistilled or rejected entirely. Solvents used should be Burdick and Jackson "distilled in glass" or equivalent quality. Note that use of chemicals of the specified grade does not eliminate the necessity of performing checks on the quality of each new batch of material used. However, use of high-quality reagents is important to minimize the probability of acquiring unsatisfactory lots of material, which would require repurification or replacement. Sodium sulfate and silica gel used in the LC separation will frequently require cleanup by extraction with organic solvent prior to use, as described in Section 9.4.4.

These controls and blanks should permit the analyst to identify the source of any background contaminant and to make corrections to the results of sample analyses. If contamination is excessive (more than 10 percent of the sample level), the source should be traced and the contamination eliminated, if possible. Note that silicones (from lubricants/sealants) and phthalates (from plastics) are major potential interferences and must be avoided entirely in collection, storage, and handling of samples for organic analysis.

APPENDIX B

PREPARATION OF XAD-2 SORBENT RESIN

APPENDIX B

PREPARATION OF XAD-2 SORBENT RESIN

B.1 SCOPE AND APPLICATION

XAD-2 resin, as supplied by the manufacturer, is impregnated with a bicarbonate solution to inhibit microbial growth during storage. Both the salt solution and any residual extractable monomer and polymer species must be removed before use. The resin is prepared by a series of water and organic extractions followed by careful drying.

B.2 EXTRACTION

B.2.1 Method 1

The procedure may be carried out in a giant Soxhlet extractor, which will contain enough XAD-2 for a single SASS module. An all-glass thimble (55-90 mm OD x 250 mm deep [top to frit]) containing an extra-coarse frit is used for extraction of XAD-2. The frit is recessed 10-15 mm above a crenulated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and stainless steel screen since it floats on the final solvent, methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse with 1 L H_2O for 1 cycle, then discard H_2O
Water	Extract with H_2O for 8 hours
Methyl alcohol	Extract for 22 hours
Methylene chloride	Extract for 22 hours
Methylene chloride (fresh)	Extract for 22 hours

B.2.2 Method 2

As an alternate to Soxhlet extraction, a continuous extractor has also been fabricated for the extraction sequence and is described in Figure B-1. This extractor has been found to be acceptable. The particular canister used for the apparatus shown in Figure B-1 contains about 500 g of finished XAD-2 or enough for more than three sorbent modules. Any size may be constructed; the choice is dependent on the needs of the sampling programs. The XAD-2 is held under light spring tension between a pair of coarse and fine screens. Spacers under the bottom screen allow for even distribution of clean solvent. The three-necked flask should be of sufficient size (3 L in this case) to hold solvent equal to twice the dead volume of the XAD-2 canister. Solvent is refluxed through the Snyder column and the distillate continuously cycled up through the XAD-2 for extraction and returned to the flask. The flow is maintained upwards through the XAD-2 to allow maximum solvent contact and prevent channeling. A valve at the bottom of the canister allows removal of solvent from the canister between changes.

Experience has shown that it is very difficult to cycle sufficient water in this mode. Therefore, the aqueous rinse is accomplished by simply flushing the canister with about 20 L of distilled water. A small pump may be useful for pumping the water through the canister. The water extraction should be carried out at the rate of about 20-40 mL/min.

After draining the water, subsequent methyl alcohol and methylene chloride extractions are carried out using the refluxing apparatus. An overnight or 10- to 20-hour period is normally sufficient for each extraction.

All materials of construction are glass, Teflon, or stainless steel. Pumps, if used, should not contain extractable materials. Pumps are not used with methanol and methylene chloride.

B.3 DRYING

After evaluation of several methods of removing residual solvent, a fluidized-bed technique has proven to be the fastest and most reliable drying method.

A simple column with suitable retainers as shown in Figure B-2 will serve as a satisfactory column. A 10.2-cm (4-in.) Pyrex pipe 0.6 m (2 ft)

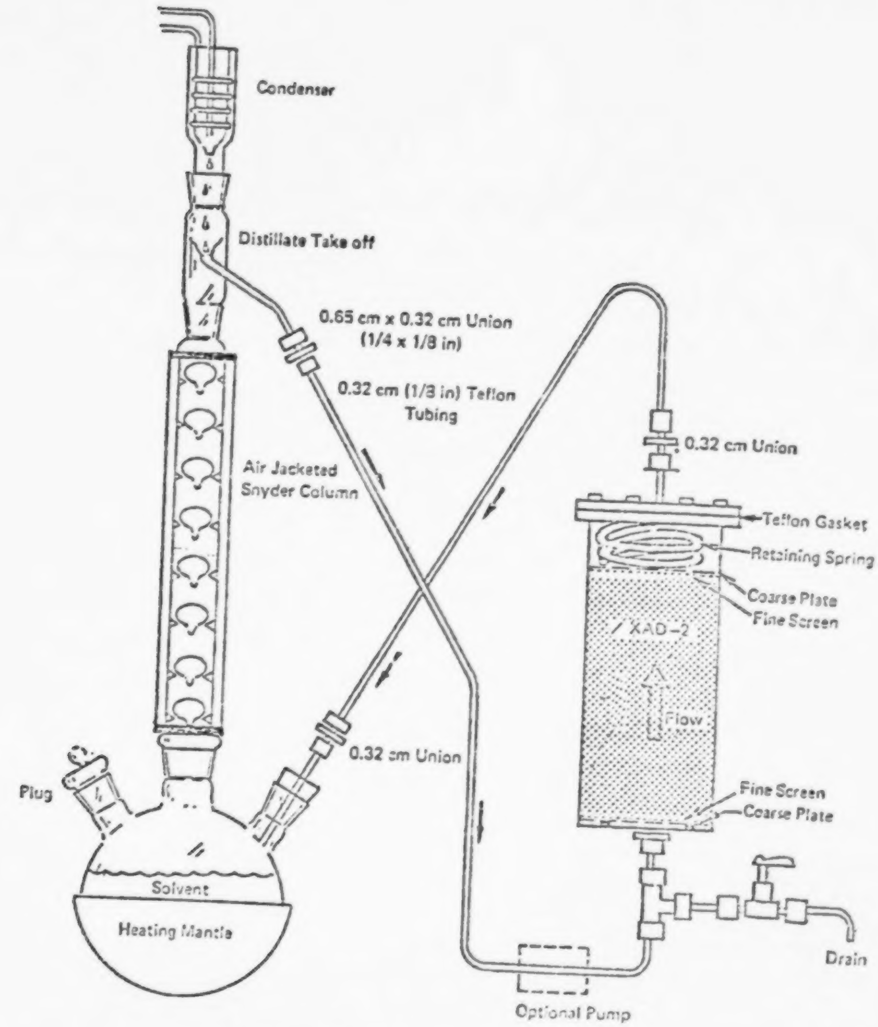

Figure B-1. XAD-2 cleanup extraction apparatus.

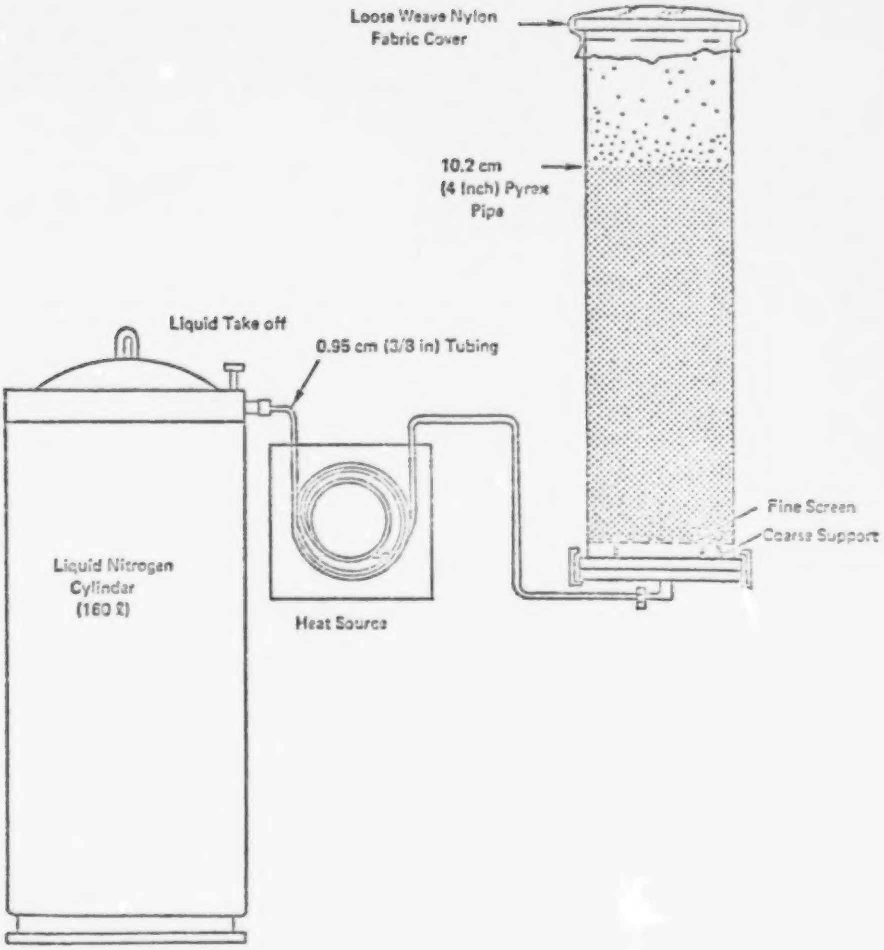

Figure B-2. XAD-2 fluidized-bed drying apparatus.

long will hold all of the XAD-2 from the extractor shown in Figure B-1 or the Soxhlet extractor, with sufficient space for fluidizing the bed while generating a minimum resin load at the exit of the column.

B.3.1 Method 1

The gas used to remove the solvent is the key to preserving the cleanliness of the XAD-2. Liquid nitrogen from a regular commercial liquid nitrogen cylinder has routinely proven to be a reliable source of large volumes of gas free from organic contaminants. The liquid nitrogen cylinder is connected to the column by a length of precleaned 0.95-cm (3/8-in.) copper tubing, coiled to pass through a heat source. As nitrogen is bled from the cylinder, it is vaporized in the heat source and passes through the column. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40° C. Experience has shown that about 500 g of XAD-2 may be dried overnight consuming a full 160-L cylinder of liquid nitrogen.

B.3.2 Method 2

As a second choice, high purity tank nitrogen may be used to dry the XAD-2. The high purity nitrogen must first be passed through a bed of activated charcoal approximately 150 mL in volume. With either type of drying method, the rate of flow should gently agitate the bed. Excessive fluidization may cause the particles to break up.

B.4 QUALITY CONTROL PROCEDURES

For both Methods 1 and 2, the quality control results must be reported for the batch. The batch must be reextracted with methylene chloride if the residual extractable organics are greater than 20 µg/mL or the gravimetric residue is greater than 0.5 mg/20 g XAD-2 extracted.

Three control procedures are used with the final XAD-2 to check for (1) residual methylene chloride, (2) extractable organics (TCO), and (3) residue (GRAV).

B.4.1 Procedure for Residual Methylene Chloride

B.4.1.1 Description--

A 1 ±0.1 g sample of dried resin is weighed into a small vial, 3 mL of toluene are added, and the vial is capped and well shaken. Five microliters of toluene (now containing extracted methylene chloride) are injected into a gas chromatograph, and the resulting integrated area is compared to a reference standard.

The reference solution consists of 2.5 µL of methylene chloride in 100 mL of toluene, simulating 100 µg residual methylene chloride on the resin. The acceptable maximum content is 1,000 µg/g resin.

B.4.1.2 Experimental--

- 6 ft. x 1/8 in. SS column containing 10% OV-101 on 100/120 Supelcoport
- Helium carrier at 30 mL/min
- FID operated on 4×10^{-11} A/mV
- Injection port temp 250° C, detector temp 305° C
- Programmed: 30° C (4 min) 40°/min 250° C (hold)
  Program terminated at 1000 seconds.

B.4.2 Procedure for Residual Extractable Organics

B.4.2.1 Description--

A 20 ±0.1 g sample of cleaned, dried resin is weighed into a precleaned alundum or cellulose thimble which is plugged with cleaned, glass wool. (Note that 20 g of resin will fill a thimble, and the resin will float out unless well plugged.) The thimble containing the resin is extracted for 24 h with 200 mL of pesticide-grade methylene chloride.*

The 200-mL extract is reduced in volume to 10 mL using a nitrogen evaporation stream. Five microliters of that solution are analyzed by gas chromatography using the TCO analysis procedure. The concentrated solution should not contain more than 20 µg/mL of TCO extracted from the XAD-2. This is equivalent to 10 µg/g of TCO in the XAD-2 and would correspond to 1.3 mg of TCO in the extract of the 130-g XAD-2 module. Care should be taken to correct the TCO data for a solvent blank prepared (200 → 10 mL concentration) in a similar manner.

B.4.2.2 Experimental--

Use the TCO analysis conditions described in the revised Level 1 manual.

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*Burdick & Jackson pesticide grade or equivalent purity.

B.4.3 Methodology for Residual Gravimetric Determination.

After the TCO value is obtained for the resin batch by the above procedures, dry the remainder of the extract in a tared vessel. There must be less than 0.5 mg residue registered or the batch of resin will have to be extracted with fresh methylene chloride again until it meets this criteria. This level corresponds to 25 μg/g in the XAD-2 or about 3.25 mg in a resin charge of 130 g.